Drop Size Distributions and Interfacial Area in Reactive Liquid-Liquid Dispersions

A Thesis submitted for the Degree

of

Doctor of Philosophy

by

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I, Achula Rajapakse, hereby declare that the work presented in this thesis, unless otherwise acknowledged is my own original work and has not been previously submitted, in whole or in part to qualify for any other academic award. I also declare that the content of the research project was carried out by me since the official commencement date of the approved research program.
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The following publications have resulted from the work performed in the present study:


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<td>reagents</td>
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<td>interfacial area, (m²/m³)</td>
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<tr>
<td>Bd</td>
<td>breath of deformed drop, (m)</td>
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<td>C</td>
<td>proportionality constant between Sauter mean maximum stable drop diameter</td>
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<tr>
<td>C₁-C₁₁</td>
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<tr>
<td>CₐCₐ</td>
<td>molar concentration of reagents A and B, (mol/m³)</td>
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<tr>
<td>Ca</td>
<td>capillary number (Gdₚμc/σ) (dimensionless)</td>
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<td>Caₐₙ</td>
<td>critical Capillary number</td>
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<tr>
<td>Caₙₘ</td>
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<tr>
<td>C₉'B</td>
<td>concentration of B in the non reactive phase, (mol/m³)</td>
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<td>concentration of B at interface in the reactive phase, (mol/m³)</td>
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<td>C₉</td>
<td>drag coefficient</td>
</tr>
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<td>Cₐ</td>
<td>impeller clearance, (m)</td>
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<td>D</td>
<td>diffusivity or diffusion coefficient, (m²/s)</td>
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<td>diffusivity of solute A in solvent B, (m²/s)</td>
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<td>Dₐ</td>
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<tr>
<td>d₃₂</td>
<td>Sauter mean drop diameter, (m or µm)</td>
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<td>d₃₂*</td>
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<tr>
<td>dₐ</td>
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<tr>
<td>dₐₙₘ</td>
<td>minimum stable drop diameter (m)</td>
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</tr>
<tr>
<td>dₐ</td>
<td>particle or drop diameter, (m)</td>
</tr>
<tr>
<td>E</td>
<td>enhancement factor (dimensionless)</td>
</tr>
<tr>
<td>Eₐ</td>
<td>activation energy of the reaction (J/mol)</td>
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<tr>
<td>Eₐₙ</td>
<td>maximum possible enhancement factor (dimensionless)</td>
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<tr>
<td>fₐ</td>
<td>fraction of conversion of A</td>
</tr>
<tr>
<td>fₐₐᵢ</td>
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<tr>
<td>g</td>
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<tr>
<td>H</td>
<td>height of liquid in the vessel, (m)</td>
</tr>
<tr>
<td>Hₐ</td>
<td>Hatta number (dimensionless)</td>
</tr>
<tr>
<td>Hₐ</td>
<td>velocity head, (m/s)</td>
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K  consistency index in a power law model, (Pa.s^n)
k  reaction rate constant (for second order, m^3/mol.s)
k_B  Boltzmann constant
k_c  continuous phase mass transfer coefficient, (m/s)
k_d  dispersed phase mass transfer coefficient, (m/s)
k_L  mass transfer coefficient, (m/s)
k_0  frequency or pre-exponential factor (for second order, m^3/mol.s)
k_p  proportionality constant
k_s  shear rate constant
k_{sc}  steady state continuous phase mass transfer coefficient, (m/s)
k_V  ratio of tangential velocity at blade tip to impeller tip speed
L  impeller blade length, (m)
L_d  length of deformed drop, (m)
L_w  London-van der Waals constant (J.m)
l  volume fraction of the phase within which A and B reacts
M  film conversion parameter (dimensionless)
M_B  molecular weight of solvent B, (kg/kmol)
MEA  monoethanolamine
M_w  molecular weight, (kg/kmol)
N  impeller speed, (rps)
N_A  number of moles of A
N_{A0}  number of moles of A present when fraction conversion is zero
N_{Fr}  Froude number (ρ_cN^2d_l^2/ΔρHg) (dimensionless)
N_p  Power number (Pg/ρN^3d_l^5) (dimensionless)
N_Q  Impeller pumping number (Q/Nd_l^3) (dimensionless)
N_sh  Sherwood number (k_c d_l / D) (dimensionless)
N_{sh_d}  Sherwood number for the dispersed phase (dimensionless)
N_{sc}  Schmidt number (μ_c/ρ_cD) (dimensionless)
N_{Re}  impeller Reynolds number (ρ_cNd_l^2/μ_c) (dimensionless)
N_{Re,p}  drop Reynolds number (ρ_c u_d/p/μ_c) (dimensionless)
n  a number, power law index
n_i  number of drop of size i
P  Power, (W)
PH833  refined mineral oil used to form the continuous phase with PIBSA
PIBSA  polyisobutylene succinic anhydride
P_v  power dissipated by the agitator per unit volume, (W/m^3)
Q  impeller pumping capacity, (m^3/s)
R  outer radius of continuous phase shell, (m)
\( R^2 \) coefficient of determination
\( R_g \) universal gas constant, J/mol.\(^\circ\)K
\( R_{\text{max}} \) maximum stable drop radius, (m)
\( R_o \) radius of solute molecule, (m)
\( r \) product formation rate (kmol/s)
\( -r_A \) rate of reaction of A or rate of disappearance of A, (kmol/s)
\( r_p \) mean drop radius, (m)
\( \text{rpm} \) revolutions per minute
\( \text{rps} \) revolutions per second
\( s \) surface element mean lifetime (surface renewal theory), (s\(^{-1}\))
\( T \) vessel diameter, (m)
\( T_m \) temperature, (\(^\circ\)K)
\( t \) time (min or sec)
\( t_L \) exposure time exposure time for a fluid element (penetration theory), (s)
\( u_t \) droplet terminal velocity, (m/s)
\( V \) volume of reactor, (m\(^3\))
\( V_A \) solute molal volume at normal boiling point, (m\(^3\)/kmol)
\( V_i \) viscosity group number
\( \text{We} \) Weber number \((N^2d_l^3\rho_c/\sigma)\) (dimensionless)

Greek symbols

\( \Delta \rho \) density difference between dispersed and continuous phase, (kg/m\(^3\))
\( \delta \) film thickness, (m)
\( \varepsilon \) rate of energy dissipation per unit mass of fluid, (W/kg)
\( \& \) extension rate, (s\(^{-1}\))
\( \phi \) dispersed phase volume fraction
\( \phi_C \) Carman’s shape factor
\( \gamma \) surface tension, (N/m)
\( \gamma \) shear rate, (s\(^{-1}\))
\( \gamma_A \) average shear rate, (s\(^{-1}\))
\( \phi \) association solvent factor
\( \lambda \) viscosity ratio \((\mu_d/\mu_c)\)
\( \mu, \mu_i \) viscosity, viscosity of i, (Pa.s)
\( \mu_{\text{app}} \) apparent viscosity, (Pa.s)
\( \nu \) kinematic viscosity, (m\(^2\)/s)
\[ \theta_c \quad \text{time between coalescence, (s)} \]
\[ \rho, \rho_i \quad \text{density, density of i, (kg/m}^3) \]
\[ \sigma \quad \text{interfacial tension, (N/m)} \]
\[ \tau \quad \text{shear stress, (N/m}^2) \]

Subscripts

- \( c \) continuous phase
- \( d \) dispersed phase
- \( i \) any substance, interface, number
- \( e, m \) emulsion or dispersion
Emulsion explosives have become the preferred choice as blasting agents for numerous industries including mining, agriculture, and construction. Today, emulsion explosives are in large scale commercial use around the world. One of the most important components in such an emulsion is an emulsifier, which controls the emulsification properties of the explosive. One such emulsifier is produced by reacting two immiscible liquids, PIBSA (polyisobutylene succinic anhydride) and MEA (monoethanolamine). The reaction is achieved by dispersing MEA into a liquid mixture that contains a mineral oil and PIBSA in a mechanically agitated reactor.

The present investigation aims to develop a greater understanding of the process involved in the production of the emulsifier. In addition, the present study aims to contribute to the current body of knowledge in liquid-liquid systems, specifically reactive systems which has had limited attention so far. The present investigation will focus on one of the key parameters that encompass liquid-liquid reactions, interfacial area. The study examines the effect of design variable such as the impeller speed, impeller type and the dispersed phase volume fraction on interfacial area.

Experiments were conducted in a 15 cm diameter, fully baffled, flat bottomed cylindrical glass vessel. Two impellers were used in the experiments, 6-bladed Rushton turbine impeller and three-bladed marine propeller. The main experimental study involves the measurement of the drop size distribution and the concentration of the reactant, PIBSA. These measurements are required to obtain the transient interfacial area of the system. Drop size measurements were conducted by sample withdrawal in conjunction with a microscopic video photographic technique. Reactant concentrations were obtained using transmission FTIR with a fixed pathlength solution cell. Impeller speeds ranging from 150 to 600 rpm and dispersed phase volume fractions, $\phi$ ranging from 0.01 to 0.028 were examined in the experimental study.

Results show that the evolution of Sauter mean drop diameter, $d_{32}$ has four different trends depending on $\phi$ and impeller speed. At high impeller speeds and high $\phi$, $d_{32}$ values decrease initially and reach constant values after a long period of time. This trend is consistent with
the findings in previous investigations. However, there are some instances where previously unreported trends can be observed in the present investigation. Under certain operating conditions, $d_{32}$ values increase initially with stirring time to reach a maximum value and then decrease to reach a steady state value. In addition, for low $\phi$, $d_{32}$ values either continuously increase with time or reach a fairly constant value after a period of agitation. The presence of these trends has been attributed to the effect of changing physical properties of the system as a result of chemical reaction. Rheological results show that transient viscosity increases at different rates depending on impeller speed and dispersed phase volume fraction.

Similar to the $d_{32}$ results, the evolution of drop size distribution also produced four distinctive trends. In fact, the trends of $d_{32}$ values provide an insight into DSD results and vice versa. For cases where $d_{32}$ decreases with time, the DSD narrows and shifts towards smaller drop sizes. When $d_{32}$ increases, the DSD broadens and shifts towards larger drop sizes. Nearly all DSDs were found to be log-normal with a peak at the low diameter side and a long tail on the large diameter side. The exception is at high impeller speeds and high $\phi$, where the DSD tends towards becoming normal distribution.

Logarithmic plot of the final steady state $d_{32}$ as a function of the impeller speed was found to be approximated by a straight line, the slope of which varies with $\phi$ and impeller type. The exponents for the impeller speed are -1.07, -1.31 and -1.19 for $\phi = 0.028$, 0.02 and 0.01, respectively, for the Rushton turbine. The corresponding values for the propeller are -0.47, -0.63 and -0.77, respectively. The final steady state DSD was found to narrow and shift toward smaller sizes with increasing impeller speed for all experimental conditions. Such result is generally found in most of the drop size studies in the literature. However, the relationship between final steady state $d_{32}$ and dispersed phase volume fraction in the present system is totally opposite to the observations reported in the literature. Results show that $d_{32}$ values decrease with increasing $\phi$. This trend could be attributed to the effect of continuous phase viscosity on the dynamics of coalescence and breakage rates.

The trends in the evolution of $d_{32}$ and DSD for the propeller are quite similar to those for the Rushton turbine. However, the propeller produces much smaller $d_{32}$ values compared to the Rushton turbine and its DSD plots are relatively narrower and on the smaller drop size side. Attempts were made to fit the final steady state $d_{32}$ data obtained in the present investigation
to existing correlations, namely those developed by Pacek et al (2001) and Kumar et al (1998). Modified Kumar et al’s (1998) correlation was found to best predict the drop size data in the present study.

Chemical analysis of the reactant mixture suggests that the conversion of PIBSA occurred exponentially for all experimental conditions. Conversions rates were found to increase with increasing impeller speed and are greater for the propeller compared to the Rushton turbine impeller. In addition, the chemical analysis results indicate that the assumption of equimolar stoichiometry is valid for this reaction. It was also found that the rate of decrease in the interfacial area increases with increasing impeller speed. This is despite the fact that higher impeller speeds produce smaller drop sizes. Furthermore, the results indicate that the interfacial area decreases at greater rate for the propeller compared to the Rushton turbine impeller. Using the reactant concentration and the drop size data, a correlation to predict the transient interfacial area of the system was obtained. The estimations of this correlation shows reasonable agreement with the experimental results under certain operating conditions: $N \leq 450$, $\phi = 0.028$. Establishment of the correlation to predict interfacial area is an important component in the development of a design equation for the emulsifier production process. However, there a number of additional components which are necessary for reactor design. Nevertheless, the study did produce some useful qualitative information for the design of the reactor used in the emulsifier production process.
This chapter provides some background information of the system that is examined in this research project. It also presents key aims and objectives that are to be addressed in the study.
1.1 **Industrial Use of Emulsion Explosives**

Explosives are used widely in numerous industries including mining, agriculture, and construction. The use of explosives has contributed largely to increase the productivity of such industries by minimising the arduous rock excavation work involved at some stages of construction and production. Many operations that are regularly carried out now with ease would not have been possible without the use of industrial explosives (Gregory, 1977). A specific example in the mining industry is the practise of drilling an array of boreholes in rock and filling them with explosives. The subsequent detonation of explosives loosens the rock and makes it readily minable (Smith and Stow, 2000). In large construction projects such as roadways and large buildings, it is not unusual to encounter rocks or other geological obstructions that are not easily removed by conventional equipment. In these instances, explosive are used to facilitate the fast progress of the projects (Day, 1989). Other applications of explosives include the preparation of machinery foundations, quarrying and excavation, recovery of minerals from mine and collieries, demolishing and general irrigation activities (Gregory, 1977).

For many years, trinitrotoluene (TNT) has been used as the preferred explosive in many industrial applications. Over time, explosives that are cost effective and less dangerous have been developed. These include ammonium-nitrate-fuel oil (ANFO) and slurry and gel explosives which overcame some of the issues encountered with TNT to a certain extent (Yinon and Zitrin, 1996). However, these explosives did have their own problems especially in applications where the explosives are likely to be in contact with water. For example, ANFO readily dissolves in water and therefore cannot be used in the presence of water. Thus the use of ANFO is generally restricted to fairly dry boreholes. Also, ANFO does not perform well in blasting hard rocks because of its low brisance and bulk energy (Binet *et al*, 1982). Usually slurry explosives do not have good water resistance properties. They also have the need to incorporate special thickening and cross-linking agents which increases their cost. In addition, they need more dangerous explosive such as TNT or pentolite for detonation (Day, 1989). In order to overcome these problems, there has been a need for an improvement in the formulation of explosives.
Discovered by Richard S Egley in 1961, emulsion explosives seemed to reduce if not completely eliminate much of the problems associated with previous formulations. Emulsion explosive remained fairly unknown for sometime immediately after its discovery, but gained significant popularity by rapid commercial development in the late 1970s (Jeffery, 1989). There are numerous advantages of using emulsion explosives. They exhibit higher water resistance compared to other explosives. They are relatively inexpensive because their primary components such as hydrocarbon fuels, water, ammonium nitrate and emulsifying agents are relatively cheaper. Also these components are less dangerous and safer to handle than those in other explosives. Emulsion explosives can be sensitised on-site (e.g. mine site) to make them detonable. This enables the components to be transported safely on public roads while complying with many strict legislative requirements applied to transport of explosives (Smith and Stow, 2000). Emulsion explosives show significant non-sensitivity to mechanical shock, flames and sparks. Certain emulsion compositions with suitable sensitization and initiation can be considered equal to dynamites because of the system's significant reactivity and high usable energy yield, as well as its effect in rock blasting (Jakubcek et al, 2002). Numerous advantages render emulsion explosives the preferred choice for many industrial application compared to other explosives. Today emulsion explosives are in large scale commercial use around the world and Figure 1.1 shows an example of one such emulsion explosive.

![Figure 1.1: Packaged emulsion explosive.](image-url)
1.2 Composition of Emulsion Explosives

An emulsion by definition is a dispersed system in which the phases are either completely immiscible or partially miscible (Shaw, 1992). Emulsions are generally classified into two types: oil-in-water (O/W) emulsion where oil droplets are dispersed in the aqueous medium of water. Conversely in the case where water droplets are dispersed in oil, the emulsion is termed water-in-oil (W/O) emulsion. Emulsion explosive compositions first disclosed by Bluhm (1969) typically comprised a discontinuous aqueous oxidizer salt solution dispersed in the form of small droplets in a continuous fuel phase. Thus emulsion explosive can be considered as water-in-oil emulsion. However, because emulsions explosives comprise very little water in the discontinuous phase, there is a suggestion that they should be correctly referred as melt-in-fuel emulsion rather than water-in-oil emulsion (Cooper et al, 1999). Since Bluhm (1969), further studies have reported improvements and variations in water-in-oil or melt-in-fuel explosives compositions (Binet et al, 1982; Bampfield, 1983; Forsberg, 1989; McKenzie and Lawrence, 1990; Chattopadhyay, 1990; Meduslac and Scales, 2000; Pearson and Morrison, 2002).

Conventional water-in-oil emulsion explosives comprise discontinuous aqueous phase comprising of discrete droplets of supersaturated aqueous solution of inorganic oxygen-releasing salts such as alkali and alkaline earth metal nitrates, chlorates and perchlorates, ammonium nitrate, ammonium chloride and ammonium perchlorate. The preferred oxidiser salt is ammonium nitrate (AN) either alone or in combination with a small quantity of calcium nitrate or sodium nitrate (Meduslac and Scales, 2000). The amount of oxidiser salt used varies generally from 45% to 94% (by weight) of the total composition.

The continuous phase of an emulsion explosive consists of water-immiscible organic fuel. The most commonly used fuels are paraffin oils and waxes, mineral and vegetable oils, petroleum, microcrystalline waxes, and other petroleum fractions. The choice of fuel or fuel mixture is determined by the demands on the rheology of the resulting explosive as well as its physical and storage stability (Jakubsek et al, 2002). Ghaicha and Leblanc’s (1995) monolayer studies on oil-water interface revealed that paraffin oil produced better results in terms of interfacial properties compared to decane. Typically the composition of organic fuel or continuous phase of the emulsion varies from 2 to 15 wt% (Cooper et al, 1999).
The emulsion phase itself is generally not considered to be an explosive. An explosive is formed when the emulsion is sensitised. In the past, sensitising was sometimes carried out by mixing the unsensitised emulsion with a powerful explosive such as trinitrotoluene or nitroglycerine. Now, however, sensitisation using powerful explosives has been virtually superseded by methods in which non-explosive sensitising agents are used. Also it is now common to sensitise an emulsion by homogeneous distribution of small void material which acts as hot spots for propagating detonation. This can be achieved through gassing using chemical agents or with the use of glass or plastic microballoons or other void materials (Smith and Stow, 2000). Once sensitised, the oxidiser and fuel phases react with one another upon initiation by a blasting cap and/or a booster to produce an effective detonation.

Figure 1.2: Structure of water-in-oil emulsion explosive (Jeffery, 1989).

Idealised structure of the emulsion is shown in Figure 1.2. The aqueous droplets assume a hexagonal shape and are closely packed. They are surrounded by a continuous oil film less than 0.0001 mm in thickness. The aqueous phase is protected from dilution by surrounding oil phase making the explosive inherently waterproof. The very small droplets relative to those found in other explosives mixtures provide a larger interfacial area resulting in a fast reaction rate with very high velocity of detonation (Jeffery, 1989).
1.3  Emulsifier in Emulsion Explosives

1.3.1  Role of the Emulsifier in Emulsion Explosives

All of the emulsion type explosive compositions contain an essential emulsifier ingredient. An emulsifier (also referred to as a surface active agent or surfactant) has many roles in an emulsion explosive. Emulsifier is required to reduce interfacial tension (and thus reducing the energy required to create new surfaces) which aids the process of drop breakage and dispersion of aqueous oxidiser phase in the continuous phase (Binet et al, 1982). Ultimately all emulsions have natural tendency to demulsify and separate into two phases since this is the state of lowest free energy (Morrison and Ross, 2002). Emulsion explosives are no exception. Without the presence of an emulsifier, the mixed phases of the compositions will soon separate to form a layered mixture which will have no utility as an explosive (Bampfield, 1983).

In water-in-oil emulsions, the emulsifier molecules orient themselves with the hydrophilic (affinity with water) head group adsorbed at the surface of the aqueous droplet and the lipophilic (affinity with oil) tail in the continuous hydrocarbon phase as shown in Figure 1.3. The emulsifier in a sense coats the droplet with a molecular layer of material reducing the rate of coalescence of dispersed phase droplets under shear.

![Figure 1.3: A lipophilic moiety of the surfactant absorbed at the surface of the water drop is effective in keeping the water drop apart in W/O emulsion (Morrison and Ross, 2002)](image)

The normal state of supersaturated aqueous phase would be crystalline. Crystallisation of oxidiser salt may occur due to excessive cooling, solid contamination or mechanical shock. It
can lead to emulsion breakdown and reduction in detonation sensitivity of the emulsion explosive (Cooper et al., 1999). The presence of the emulsifier layer around the droplet acts as an impermeable barrier between the droplets which stops crystals growing from one droplet into another droplet. Emulsifiers used in an emulsion explosive are required not only to facilitate the emulsification process but also to prevent the crystallisation and coalescence of the oxidiser phase. Thus the performance of emulsion explosives is crucially dependent on the activity of the chosen emulsifying agent.

### 1.3.2 Emulsifiers Used in Emulsion Explosives

Emulsion explosives comprising a large volume of nitrate salt solution finely dispersed in a small volume of hydrocarbon oil require surfactant with low HLB (hydrophobic-lipophilic balance) values such as sorbitan mono oleates or various polymeric surfactants (Ghaicha and Leblanc, 1995). One of the first emulsifiers used in emulsion explosives were simple sorbitan mono oleates. However, these emulsifiers did not provide sufficient long term stability. Further research led to the formation of various soaps and oxazoline as emulsifiers but these emulsifiers were not compatible with the internal and external stabilizers in ammonium nitrate which often cause the emulsions to break down and fail to detonate (Pearson and Morrison, 2002). These emulsifiers were followed by another class of emulsifiers known as polyisobutenyl succinic anhydride derivatives (PIBSA derivatives) which are more compatible with the stabilizers in ammonium nitrate and other single salts in explosive emulsion formulae.

The lipophilic moiety of these emulsifiers can be derived from PIBSA and the hydrophilic moiety (polar in character) can be derived from various chemicals including alcohols, polyol, amines and alkanolamines which form an adduct with PIBSA. Typically the emulsifier comprises up to 5 wt % of the emulsion. Higher proportions of the emulsifier may be used. It may serve as a supplementary fuel for the composition but in general it is not necessary to add more than 5 wt % of the emulsifying agent to achieve the desired effect (Smith and Stow, 2000).
The choice of emulsifier is primarily based on the composition of the emulsion explosive which in itself vary depending on the application. Variety of emulsifier types and blends has been disclosed by numerous patents. Baker and Cooper (1989) reported an emulsion explosive composition in which the emulsifier is a reaction product of PIBSA and amines such as ethylene diamine, diethylene tetramine and mono and di-ethanolamine. Binet et al (1982) reported an emulsion containing an emulsifier with PIBSA as a hydrophobic moiety and polyethylene glycol or polyethylenimine as a hydrophilic moiety. An emulsifier produced from a reaction between PIBSA and urea was reported by Boer (2003). In some applications, mixtures or blends of emulsifiers were used (Bampfield, 1983; Chattopadhyay, 1990; Nguyen, 1991; Cooper et al, 1999; Pearson and Morrison, 2002). Ghaicha and Leblanc (1995) observed that smaller drops and maximum emulsion stability could be achieved by a combination of PIBSA derivative emulsifiers and sorbitan mono oleate.

1.3.3 Production of the Emulsifier

During the 1970s and 1980s, the use and production PIBSA derivative emulsifiers increased as it gained a reputation as superior emulsifiers for emulsion explosives (Boer, 2003). Currently popular emulsion explosives generally contain emulsifiers produced from reactions between PIBSA and monoethanolamine or diethanolamine (Cooper et al, 1999; Meduselac and Scales, 2000; Nguyen, 1991; Smith and Stow, 2000; Boer, 2003). The present study will focus on the production of an emulsifier produced by the reaction of PIBSA and monoethanolamine.

1.3.3.1 Monoethanolamine

Monoethanolamine (2-aminoethanol), also known as MEA, belongs to the class of chemicals known as alkanolamines or amino alcohols. Commercial manufacture of MEA started in 1931. Today MEA is produced mostly by the reaction of ethylene oxide and ammonia (Weast and Astle, 1985).
Alkanolamines are bifunctional molecules because they contain both alcohol and amine functional groups in the same compound. This allows them to react with a wide variety of chemicals such as acids, fatty acids and esters, acyl halides, acid anhydrides, aldehydes and ketones, alkyl and aralkyl halides (Kroschwitz, 1992). MEA is used in a wide variety of industrial applications such as adhesives manufacture, wire coatings, corrosion inhibitors, wood pulping, emulsion stabilisers, and detergents manufacture. Possibly the most common use of MEA would be in natural gas purification (Shahi et al., 1994; Li and Lie, 1994; Alejandre et al., 2000). Thus MEA is often recognised as the low cost solvent used in the removal of acidic gases such as CO$_2$ and H$_2$S from natural gas.

### 1.3.3.2 Polyisobutylene Succinic Anhydride (PIBSA)

PIBSA has been produced for more than half a century as a major raw material for the synthesis of ashless dispersants, which are an important class of lubricating oil additives. PIBSA is prepared in the reaction of either BF$_3$-catalysed or AlCl$_3$-catalysed polyisobutylene (PIB) with maleic anhydride via a thermal ene reaction (Harrison et al., 2002).

![PIB + Maleic Anhydride ➔ PIBSA](image)
As shown in Figure 1.5, PIBSA molecule contains a branched PIB chain attached to an anhydride ring. Apart from the production of emulsifier for emulsion explosives, PIBSA is used in a number of other applications such as the production of polymeric surfactants used for oil spill dispersants (Al-Sabagh and Atta, 1999), uranium extraction (Bock and Vallint Jr, 1982), and production of automotive engine lubricant additives (Papke and Robinson, 1994; Tomlinson et al, 1997; Harrison et al, 2002).

The molecular mass of PIBSA can vary significantly depending on the molar mass of PIB used in its synthesis. PIBSA having an average molecular weight in the range of 400 to 5000 has been specifically identified to be the useful for emulsion explosives (Forsberg, 1989). Boer (2003) suggests that one preferred embodiment is the one with a molar mass of 1000. PIBSA derived emulsifiers having an average molecular weight of 1050 were found to perform better in terms of producing smaller droplets and more stable emulsions compared to lower molecular weight derivatives (Ghaicha and Leblanc, 1995).

### 1.3.3.3 PIBSA derivative emulsifier

Based on the earlier concept of producing ashless dispersants for automotive lubricating oils, Baker (1988) discovered a class of anionic surfactants that include the derivatives of alkenylsuccinic acid or anhydride. He suggested that the surfactant or emulsifier produced by reacting PIBSA and MEA was useful for systems consisting oil and aqueous phase. PIBSA derivative emulsifier is typically produced by reacting the PIBSA and MEA under mild conditions as per the reaction scheme shown below:

![Reaction scheme](Image)

**Figure 1.6:** Reaction scheme that represents the formation of the PIBSA derivative emulsifier.
At low temperatures, anhydride ring opens with the formation of the derivative containing amide functional group which is then partially rearranged to form the derivative containing ester functional group. The resulting mixed ester/amide derivative is the emulsifier (McKenzie and Lawrence, 1990). Further heating of the product can convert amide derivatives to imide. Depending on the reaction conditions, mixed derivative (amide/ester and imide) are also possible.

Numerous patents have highlighted the usefulness of the PIBSA derivative emulsifiers in emulsion explosives (Nguyen, 1991; Cooper et al, 1999; Meduselac and Scales, 2000; Smith and Stow, 2000). In addition, many research studies have been carried out examining the surface chemistry of the emulsifier or similar derivatives. Gaicha et al (1992) and Chottopadhyay et al (1993) examined the effect of branching of PIBSA chain and the performance of the derivatives as a surfactant in a medium containing ammonium nitrate. Ghaicha and Leblanc (1995) conducted monolayer studies at oil-water interface examining the effect of PIBSA chain length on emulsion properties. Chottopadhyay et al (1992) conducted a similar investigation but with double-tailed surfactants. Reynolds et al (2003) examined various combinations of imide/amide derivatives of PIBSA and their effects on the HLB.

The literature mentioned above, however, reveals very little regarding the reaction kinetics and the reactor involved in the production of the PIBSA/MEA derivative emulsifier. This suggests that there is significant lack of knowledge on the production of emulsifier although it is produced in quite large quantities around the world. This study aims to develop a greater understanding of reactor design aspects which will lead to the optimisation of PIBSA derivative emulsifier production operation.
1.4 Aims and Objectives of the Research Project

Reactive components involved in the emulsifier production, MEA and PIBSA, are immiscible liquids. The reaction is achieved by dispersing MEA in PIBSA-hydrocarbon oil mixture through mechanical agitation. This system falls into the category of reactive heterogenous liquid-liquid system. It is well known that dynamic behaviour of liquid-liquid reactions is complex due to fact both mass transfer and chemical reaction occur simultaneously (Zaldivar et al, 1996). Paul et al (2004) suggested that liquid-liquid reactor design involves one of the most difficult mixing problems. In the absence of chemical reactions, the mass transfer rate in liquid-liquid systems is determined by the mass transfer coefficient and interfacial area. When a multiphase reaction occurs, in addition to the influence of mass transfer coefficient and interfacial area, the effect of the chemical reactions on the overall rate of conversion must also be taken into consideration (Bourne, 2003). The interdependence of these phenomena means it is quite difficult to study each item in isolation.

This study examines the production of polyisobutylene succinic anhydride derivative emulsifier in a reactive heterogenous liquid-liquid system and aims to develop a greater understanding of the reactor design leading to the optimisation of the batch reaction process. Specific research objectives of the present research are:

- To develop an experimental technique to measure the transient drop sizes in the reactive liquid-liquid system. Many past studies involving drop size measurement dealt mainly with non-reactive dispersions. As such, developing a drop size measurement technique for a reactive dispersion can be considered to be quite novel.

- To identify the relationship between variables such as the agitation intensity, dispersed phase volume fraction, continuous phase viscosity and impeller type on the size distribution of droplets during the reaction.

- To develop a mathematical model for predicting the drop size distribution as a function of various parameters that influence it.
• To develop quantitative techniques for determining the concentration of one or all reactants during the reaction period. Numerous chemical analysis techniques exist for these compounds but majority of them have not been used for quantitative analysis.

• To identify the factors influencing the reactant conversion rate and to develop predictive correlations between them and conversion rate.

• To use the drop size and concentration data to develop a correlation to predict the transient behaviour of interfacial area at various operating conditions.

• To make recommendations to optimise the production of the PIBSA/MEA derivative emulsifier.
This chapter reviews the literature related to heterogeneous reactions, specifically agitated liquid-liquid dispersions. Subjects discussed include some aspects of interfacial mass transfer, mass transfer coefficients, reaction kinetics, interfacial area and reactor design. Primary focus however would be on the topic of interfacial area and drop size distribution in agitated systems.
2.1 Liquid-liquid Reactions

Fluid phase heterogeneous reactions have an important role in chemical industry. In these systems the chemical compounds are present in distinct phases and mass transfer occurs between them by diffusion and/or convection, simultaneous to reaction (Quadros et al., 2004). Examples of industrial processes involving liquid-liquid reactions include: production of caustic soda by reaction of sodium amalgam and water, nitration of organic compounds with aqueous nitric acid, sulphur removal from petroleum fraction by aqueous ethanolamines and treatment of petroleum products with sulphuric acid (Wales, 1989). In the present investigation one of the reactants, PIBSA, is present in the continuous phase and the dispersed phase contains the other reactant, MEA. For the reaction to occur, MEA must diffuse into the continuous phase before it can react with PIBSA. Consequently, in addition to chemical reaction rates, certain physical factors which affect the rate of mass transfer between phases also affect the overall conversion. These include the size of interfacial area, rate of diffusion across the interfacial film, and rate of diffusion of the products away from the reaction zone (Wales, 1989). The latter is of importance only with reversible reactions, unless the concentration of the product is sufficiently high to influence the diffusivities of the reactants. Nevertheless, a complete formulation of the overall rate equation must take into account both of the mass transfer and chemical reaction rates.

In heterogeneous liquid-liquid systems, chemical reaction and mass transfer occur simultaneously. Therefore the analysis of these systems is complicated by the fact that these two processes interact. Mass transfer can be increased if the substance transferred into the other phase reacts there chemically. Vice versa, the chemical reaction can be slowed down by mass-transfer resistance, leading to a lower reaction rate (Zaldivar et al., 1995). The interaction between chemical reaction and mass transfer is governed by the relative rates of the two processes. In some instances, one of the rates is much smaller than the other that it becomes the controlling one. Very fast chemical reactions are mass transfer controlled whereas very slow chemical reactions are kinetics controlled (Paul, 2004). Experimentally, the dominant mechanism can be detected by observing the effect of certain changes in operating conditions on conversion. If the overall conversion rate increased markedly with temperature in accordance with the Arrhenius law, the rate is kinetics controlled. One the other hand, if the conversion rate changes when the size of interfacial area or the flow rate is
varied, then the rate is mass transfer controlled (Wales, 1989). If system is deemed to be purely mass transfer or reaction controlled, then the determination of the overall rate equation is greatly simplified. However, in reality, very few reactions can strictly be classified as one or the other.

### 2.1.1 Interfacial Mass Transfer

The theoretical treatment of heterogenous liquid-liquid reactions follows from the extension of well known theories of interfacial mass transfer, namely the film theory, penetration theory and surface renewal theories (Laddha and Degaleesan, 1976).

#### 2.1.1.1 Film Theory

Developed by Whitman (1923), film theory is the earliest and simplest theory for interfacial mass transfer (Hines and Maddox, 1985). The film model is based on the assumption that mass transfer occurs by molecular diffusion in a film next to the interface. Beyond the film, bulk liquid, the molecular diffusion is assumed to be negligible compared to the turbulent diffusion (Alopaeus, 2001). This results in a constant concentration in the bulk. As shown schematically in Figure 2.1, entire resistance to mass transfer reside in the stagnant liquid film. Thus the mass transfer coefficient, $k_L$, is proportional to the diffusion coefficient, $D$, and film thickness, $\delta$:

$$k_L = \frac{D}{\delta} \quad (2.1)$$

This film thickness is almost never known priori, but must be found from measurements of $k_L$ and $D$ (Cussler, 1984). Given that mass transfer coefficient varies in some fashion with flow conditions of the system, the thickness of the film can be considered to be a function of variables such as fluid viscosity and stirring rates.
2.1.1.2 Penetration Theory

In order to describe the physical process more accurately (than the film theory), Higbie (1935) suggested a penetration theory for interfacial mass transfer (Hines and Maddox, 1985). The theory assumes that the liquid surface consists of small fluid elements that contact the interface for an average time after which they penetrate into the bulk of the liquid. Each element is then replaced by another element from the bulk liquid phase. Consider Figure 2.2, in which solute A diffuses with the element from the gas-liquid interface into the bulk liquid.
The penetration theory predicts that the mass transfer coefficient, $k_L$, is proportional to the diffusion coefficient, $D$ and the exposure time for a fluid element, $t_L$.

$$k_L = 2\left(\frac{D}{\pi t_L}\right)^{0.5} \tag{2.2}$$

### 2.1.1.3 Surface Renewal Theory

The surface renewal theory extends the penetration theory and assumes that the time of contact is not constant, but an average exposure time determined from an assumed time distribution. Danckwerts (1951) suggested that the chance of an element being replaced on the interface is independent of the time for which it has been exposed (Hines and Maddox, 1985). Thus the interface is very much like a mosaic of fluid elements of different exposure times. Mass transfer coefficient for the surface renewal model is expressed by the following relationship:
2.1.2 Overall Rate Equations for Liquid-liquid Reactions

As mentioned above, the overall conversion rate has contributions from mass transfer and reaction kinetics. Thus the formulation of an overall rate equation for heterogeneous reaction is extremely complex. Nevertheless, various authors have provided some useful analytical solutions for the rate equation for gas-liquid reactive systems. However, these concepts hold equally true for liquid-liquid reactions. Astirita (1967), Levenspiel (1972), and Doraiswamy and Sharma (1984) described an effective framework to evaluate the relative contributions of mass transfer and reaction kinetics in heterogeneous systems (Paul et al., 2004). Depending on the relative rates of mass transfer and chemical reaction, heterogeneous systems are classified into different regimes. The classification of regimes allowed rate equations to be simplified, which in turn eased the development of analytical solution for the problem. Bourne (2003) classified reaction into four different regimes: very slow reactions, slow reactions, fast reactions and instantaneous reactions. These will be discussed in detail in the following section of this chapter. Levenspiel (1979) described five reaction regimes instead four, whereas Nanda and Sharma (1968) considered six regimes. Bourne (2003) and Doraiswamy and Sharma (1984) proposed several subsets within their four regimes. In general, the compilation of these rate equations is similar for all cases.

Fundamental concepts and rate equations are generally developed for a single chemical reaction having second order (Bourne, 2003). The following discussion on reaction regimes and respective rate equations will also be based on such condition. Consider the following second order reaction:

\[ A + B \rightarrow P \]  \hspace{1cm} (2.4)
where are A and B are reactants initially present in the continuous and dispersed phases respectively, and P is the product. Given that the reaction is an irreversible second order reaction with the order being one with respect to both A and B, the reaction rate equation can be written as:

\[-r_A = kC_A C_B\]  

(2.5)

For the purpose of this discussion, A is present in phase 1 (dispersed phase) and B is present in phase 2 (continuous phase) and will be labelled as such in the concentration diagrams shown later. Given that reactant A must travel from phase 1 to phase 2 for the reaction to occur, diffusion resistances enter the rate equation (Levenspiel, 1979). As such the concepts of interfacial mass transfer discussed in the earlier section will be of use. Much of theoretical development of rate equations are based on Whitman’s (1923) film theory because it is easier to develop and use as compared to other theories (Levenspiel, 1972). Other theories, namely Higbie’s penetration theory (1935) and Danckwerts’ surface renewal theory (1951) can also be used and would essentially give the same results. Quadros (2004) used both the film and penetration theories to model the heterogeneous liquid-liquid reaction of benzene nitration in an intermediate regime and found that both were adequate to model the industrial system, although film model allowed for a simpler mathematical treatment. Figure 2.3 shows the concentration profile in two film theory. It depicts the resistance to mass transfer located in the film of each phase located on either side of the interface.
Several forms of the rate equation can result depending on the relative values of the rate constant $k$, mass transfer coefficients $k_c$ and $k_d$, and the concentration ratio of the reactants $C_A/C_B$. An overall rate expression which accounts for all these factors can be written as follows (Levenspiel, 1979):

$$r = \frac{C_B}{\frac{1}{k_d a} + \frac{H_A}{k_c a} + \frac{H_A}{klC_A}}$$  \hspace{1cm} (2.6)
where \( r \) = rate of formation of products, mol/s
\( k \) = second order rate constant, m\(^3\)/mol.s
\( C_A \) = bulk concentration of A, mol/m\(^3\)
\( C_B \) = bulk concentration of B, mol/m\(^3\)
\( l \) = volume fraction of the phase within which A and B reacts (for this particular system, the continuous phase)
\( a \) = interfacial area, m\(^2\)/m\(^3\)
\( k_d \) = dispersed phase mass transfer coefficient, m/s
\( k_c \) = continuous phase mass transfer coefficient, m/s
\( H_A \) = distribution coefficient

Equation (2.6) shows that dispersed and continuous phase films and the bulk of the continuous phase act as resistances in series. Some resistances can be negligible compared to others which lead to a simplified overall rate equation. Depending on the location of the reaction these resistance have varying degrees of impact on the overall rate. Reaction can occur (i) at the interface between phases (ii) near the interface, but within the diffusion layer (or film) of the continuous phase and (iii) in the bulk of the continuous phase far removed from the interface (Bourne, 2003). Depending on the location of the reaction, interfacial reactions can be classified into several different regimes: very slow reaction, slow reaction, fast reaction and instantaneous reaction. To identify the reaction regime in heterogeneous reactions the Hatta number, \( Ha \) is used (Quadros et al., 2004).

### 2.1.2.1 Hatta Number

The dimensionless Hatta number, \( Ha \) is used to characterise the different reaction regimes. It is essentially the square root of the ratio between the diffusion time and reaction time. The number is defined as:

\[
Ha = \sqrt{\frac{kC_A D_B}{K_L}}
\]  

(2.7)
When the concentration of A is much higher than the solubility of B in phase 2 ($C_A >> C_{B_1}$), the reaction rate will be pseudo first order in B, the rate constant being $kC_A$. A time constant for the consumption of B in the film is then $(kC_A)^{-1}$. Transport of B through the film is by molecular diffusion for which Fick’s second law gives a time constant of $(\delta^2/D_B)$. Under conditions where diffusion is fast relative to reaction, hardly any reaction occurs in the film. This occurs when:

$$\delta/D_B << (kC_A)^{-1} \quad \text{or} \quad kC_A\delta^2 << 1 \quad (2.8)$$

Using the definition of $k_L (=D/\delta)$ it has become a common practice to write the dimensionless group as shown in equation (2.7). As such when Ha $<< 1$, reaction does not occur in the film. On the other hand when Ha $>> 1$, some reaction does occur and the regime cannot be slow. Furthermore, it had been widely suggested that Ha $< 0.3$ signifies no reaction in the film (Bourne, 2003; Zaldivar et al, 1996). In addition Ha $> 3$ signifies complete reaction in the film and as such these reactions are classified as fast or instantaneous reactions (Bourne, 2003). Zaldivar et al (1996) and Quadros et al (2004) used the following criterion of Ha for identifying respective reaction regimes:

- Slow reactions - Ha $< 0.3$ (complete reaction in bulk)
- Intermediate reaction – $0.3 > Ha < 2$
- Fast reactions – Ha $> 2$ (complete reaction in film)

Levenspiel (1972) employed a so called “film conversion parameter”, M to determine the regime of a specific heterogeneous reaction. It is the ratio of the maximum possible conversion in film and that of the maximum diffusion transport through the film. The parameter is defined as:

$$M = \frac{kC_A D_B}{k^2_L} \quad (2.9)$$

When compared to the definition of Ha, it can be clearly seen that M=$Ha^2$. Despite that fact both parameters (Ha and M) characterise reactions in the same manner, Levenspiel (1972) provided more comprehensive criterion to characterise various reaction regimes using M.
• If $M > 4$, reaction occurs in the film and the reaction is either fast or instantaneous.

• If $0.0004 < M < 4$, the reaction is classified as intermediate. In this regime, the reaction occurs in the film as well as in the bulk of the continuous phase.

• If $M < 0.0004$, reaction occurs in the bulk of the continuous phase and is considered to be a slow reaction.

### 2.1.2.2 Reaction Regimes and Rate Equations

**Regime 1: Very slow reactions**

Reaction rate in this regime is much slower than the mass transfer rate. As such the reaction is not affected by the mixing and mass transfer rate (Paul *et al.*, 2004). Only very poor bulk or macromixing (i.e. solids settled on the bottom or large dispersed phase drop size) could result in slow conversion. If the reaction is very slow, B saturates the continuous phase and $C_B = C_{Bi}$, so that there is no concentration gradient of B in dispersed phase as shown in the concentration profile of the reaction regime in Figure 2.4. The rate of formation of the product is determined by the kinetics of the chemical reaction. This can be expressed as:

\[
    r = k_{f} C_{A} C_{B} \tag{2.10}
\]

Variables characterising mass transfer such as mass transfer coefficient $k_L$, dispersed phase volume fraction $\phi$, and interfacial area $a$, are not required in the equation for very slow reaction regime.
Regime 2: Slow reactions

Here the reaction is sufficiently slow, it does not take place in the continuous phase film, but B diffuses across the film and reacts with A in the bulk of the continuous phase (Bourne, 2003). The concentration profile for slow reactions (Figure 2.5) shows the concentration difference driving this diffusion is to be \((C_{B_i} - C_{B})\). In cases where phase 1 is pure, \(C_{B_i} = C_{B_i}'\), and the term \((1/k_d a)\) in the rate equation (2.6) vanishes. Furthermore, if the distribution coefficient \(H_A\) is very high (B is much more soluble in phase 1 than in phase 2, where the reaction occurs), the term \((1/k_d a)\) vanishes. In such cases the rate equation (2.6) is simplified to give:

\[
r = \frac{C_B}{\frac{1}{k_C a} + \frac{1}{k_l C_A}} \tag{2.11}
\]

Another case would be where reaction is sufficiently fast that \(C_B = 0\), but not so fast that B reacts in the continuous phase film region. In this case equation (2.11) is simplified further to produce:

\[
r = k_C a C_B \tag{2.12}
\]
Here the reaction rate depends entirely on the rate of mass transfer across the film of phase 2 (i.e. continuous phase).

![Figure 2.5: Concentration profiles in slow reaction regime (Bourne, 2003).](image)

**Regime 3: Fast reactions**

Here the reaction is sufficiently fast so that the diffusing substance B reacts completely within the diffusion film (Figure 2.6). When the concentration of A in phase 2 greatly exceeds the solubility of B in this phase (i.e. when \( C_A >> C_{Bi} \)), the concentration of A is almost constant in the film despite its consumption by the reaction. Sharma and Nanda (1968) classified this particular type of case being “very fast reaction without depletion”. In this situation the reaction becomes pseudo-first order in \( C_B \) throughout the film and the reaction rate can be then expressed as:

\[
r = a(kD_B C_A)^{1/2} C_{Bi}
\]

(2.13)

It should be noted that equations (2.13) and (2.14) are valid for the condition where \( C_A/C_{Bi} >> Ha \). If this condition is not satisfied, but \( Ha > 3 \) (complete reaction in the film), then the reaction in the film has second-order kinetics (i.e. \( C_A \) is not uniform), and a numerical solution for the reaction rate is required. Sharma and Nanda (1968) classified this as “very
"fast reaction with depletion”, where the reactant is depleted near the surface, but the reaction is not fast enough to be treated as instantaneous. In the film, $C_A$ will be essentially constant if the maximum rate of transfer of $A$ into the film $(k_c a C_A)$ is much greater than its maximum rate of consumption there $(a(k C_A D_B)^{1/2} C_{Bi})$. Rearranging these terms, equation (2.13) can be written as:

$$r = k_L a C_{Bi} H a$$  \hspace{1cm} (2.14)$$

The term $(k_c a C_{Bi})$ is the maximum rate of diffusion of $B$ across the film in phase 2 in the absence of reaction, in which case $C_B = 0$. Equation (2.14) shows enhancement of this rate by the factor $Ha$ when reaction in the film is complete and $C_A$ is uniform. For the reaction in the transition region between regimes 2 and 3, the rate equation can be expressed as:

$$r = k_L a C_{Bi} \left(1 + H a^2 \right)^{1/2}$$  \hspace{1cm} (2.15)$$

Sharma and Nanda (1968) classified this type of reactions as being “fast reaction without depletion” and Levenspiel (1979) classified this as “intermediate reaction”. Here only a part of $B$ reacts in the film, whilst the rest reacts in the bulk of phase 2.

Figure 2.6: Concentration profiles in fast reaction regime (Bourne, 2003).
**Regime 4: Instantaneous reactions**

The term instantaneous signifies that the time scale of chemical reaction is extremely short relative to that of the diffusion through the liquid film. The reactants A and B do not coexist anywhere, but react as soon as they encounter each other at the position $z$ in the diffusion film (Figure 2.7). When the resistance in phase 1 is negligible ($H_A k_f >> k_f$), then $C_B = C_{B1}$ and the rate equation for instantaneous reactions can be written as:

$$r = k_c a C_{B1} \left(1 + \frac{D_A C_A}{D_B C_{B1}}\right)$$  \hspace{1cm} (2.16)

In the absence of chemical reaction and of resistance to mass transfer in phase 1, the rate of transfer of B into phase 2 is $k_c a (C_{B1} - C_B)$. This is highest when $C_B = 0$ and equal to $k_c a C_{B1}$. Thus it can be seen that a reaction in the film enhances (or accelerates) the maximum physical mass transfer rate by the factor $\left(1 + \frac{D_A C_A}{D_B C_{B1}}\right)$. In the case for fast reactions (regime 3) the enhancement was by a factor of $H_a$.

![Figure 2.7: Concentration profiles in instantaneous reaction regime (Bourne, 2003).](image)
Zaldivar et al (1996) denote the enhancement rate by an enhancement factor, E. It can be calculated by trial and error using the equation:

\[
E = \frac{Ha \sqrt{(E_E - E)/(E_E - 1)}}{\tanh Ha \sqrt{(E_E - E)/(E_E - 1)}} \times \left(1 - \frac{C_B}{C_B \cosh Ha \sqrt{(E_E - E)/(E_E - 1)}}\right) \quad (2.17)
\]

In fast reactions \( E = Ha \), whereas for instantaneous reactions the maximum possible enhancement factor \( E_\infty \), is given by:

\[
E_\infty = 1 + \frac{D_A C_A}{D_B C_B} \quad (2.18)
\]

The overall rate equations presented in this chapter have been for a single irreversible reaction taking place in the continuous phase whose kinetics is first-order for each of reactive components. Extension of the general principle to other reaction orders, multiple reactions, reversibility etc. are available in literature (Doraiswamy and Sharma, 1984; Laddha and Degaleesan, 1976; Trambouze et al, 1988). Four types of reaction regimes including several subsets within these regimes were discussed and respective rate equations were provided. Often in a heterogeneous reactor, the reaction does not strictly fit into one of these regimes throughout the course of its operation. The reaction regime can change as the reaction progresses. For example, if reactant A is gradually consumed in phase 2 causing \( C_A \) to decrease, the solubility of B in the phase can change as reaction product accumulates in phase 2 (Bourne, 2003). Zaldivar et al (1995, 1996) was able to conduct experiments in different regimes by modifying the concentration of one of the components of the system (the sulphuric acid strength).

The overall rate equations take a number of forms in accordance with the reaction regime (and the location of the reaction) and each of these expressions require knowledge of a number of variables including mass transfer coefficient, diffusion coefficient, interfacial area and reaction kinetics. Determination of these factors for liquid-liquid systems will be discussed in the following sections of this chapter.
2.1.3 Mass Transfer Coefficient

The rate of mass transfer between two liquids brought into intimate contact in a mixing vessel is dependent upon the concentration difference, the interfacial area between the two liquids, and the mass transfer coefficient (Skelland and Moeti, 1990). Comprehensive correlations of mass transfer coefficient and interfacial area are therefore essential for the optimum design and scale-up of liquid-liquid reactors.

There have been relatively few studies on mass transfer coefficients for liquid-liquid systems in agitated vessels. Continuous phase mass transfer coefficient was studied by Schindler and Treybal (1968) and Keey and Glen (1969) for continuous flow stirred tanks, and by Skelland and Lee (1981) and Skelland and Moeti (1990) for a batch stirred system. In comparison, there have been fairly extensive studies of mass transfer in other heterogeneous systems such as gas-liquid and solid liquids systems (Treybal et al., 1981). Hiraoka et al (1990) found that the mass transfer behaviour of tiny droplets was very similar to that of solid spheres. They found that the mass transfer coefficient for tiny droplet satisfied the correlations for solid spheres. Thus the correlations developed for solid-liquid systems could be useful for determining mass transfer coefficients in agitated liquid-liquid systems.

2.1.3.1 Continuous Phase Mass Transfer Coefficient

Agitated liquid-liquid systems

Schindler and Treybal (1968) measured the area free continuous phase mass transfer coefficients for continuous flow of ethyl acetate dispersed in water. Agitation was provided by flat bladed turbines for baffled and unbaffled vessels. Specific interfacial area was determined by light transmission technique (calibrated by photography) which permitted a vertical traverse of the vessel. An unsteady-state diffusion model for a continuous phase stagnant shell around each drop was employed to deduce the expression:
Chapter 2

\[ k_c = \frac{D_A R}{(R-r_p)r_p} + \sum_{n=1}^{\infty} \frac{2(R-r_p)}{N n^2 \pi^2 \theta_c} \left[ 1 - \exp\left( -\frac{n^2 \pi^2 D_A \theta_c}{(R-r_p)^2} \right) \right] \] (2.19)

where \( k_c \) = continuous phase mass transfer coefficient, m/s
\( D_A \) = diffusivity of A, m²/s
\( R \) = outer radius of continuous phase shell, m
\( r_p \) = mean drop radius, m
\( \theta_c \) = time between coalescence, s
\( n \) = a number

The first term on the right is a steady state coefficient and the second a transient term. The authors stated that the derivation was unrealistic in that it assumes only molecular diffusion, no circulation of the fluid around the drop, no drop oscillation, and no slip or fluctuating velocities. Therefore a general expression from equation (2.19) can be written as:

\[ k_C = k_{sc} + \text{const.} \left( \frac{D_A}{\theta_c} \right)^{0.5} \] (2.20)

The steady state mass transfer coefficient, \( k_{sc} \) might be estimated by the correlation proposed by Harriott et al (1962) because it involves particles of the same size range as the droplets and it agrees best with the mass transfer coefficients observed at low impeller Reynolds numbers (Schindler and Treybal, 1968). Using the correlation recommended for \( k_{sc} \), the average constant of equation (2.20) was found to be 3.94 for runs conducted under baffled conditions.

Keey and Glen (1969) investigated the continuous phase mass transfer coefficient in an agitated extraction system in continuously operated baffled vessels with various sizes of six-bladed paddles and vessel diameters. The dispersed and the continuous phases were iso-octane and water respectively with o-nitrophenol as the solute. Drop sizes were measured using photography. Based on the assumption that the drops were surrounded by turbulent boundary layers, the following expression was derived:

\[ N_{St} \propto N_{Re}^{-1/8} N_{Sc}^{1/2} \] (2.21)
This expression was developed on the basis that for an impeller Reynolds number range between $10^4$ and $10^5$ where the drag coefficient is a weak function of the Reynolds number. A general correlation was obtained for the all data in their work:

$$N_{sh} = \frac{k_c d_I}{D_A} = 8.92 \times 10^{-4} N_{Re}^{1.36} T^{-0.5} d_I^{-0.36} - 336 \quad (2.22)$$

where $N_{sh} = \text{Sherwood number}$

$N_{Re} = \text{impeller Reynolds number} \left(\frac{\rho_c N d_i^2}{\mu_c}\right)$

$D_A = \text{diffusivity of A, m}^2/\text{s}$

$T = \text{vessel diameter, m}$

$N = \text{impeller speed, rps}$

$d_I = \text{impeller diameter, m}$

$k_c = \text{continuous phase mass transfer coefficient, m/s}$

$\rho_c = \text{continuous phase density, kg/m}^3$

$\mu_c = \text{continuous phase viscosity, Pa.s}$

This correlation which includes the influence of vessel geometry and the mass transfer coefficients was based on the assumption of no mixing occurring in the dispersed phase.

Investigations by Schindler and Treybal (1968) and Keey and Glen (1969) were limited to systems they have studied, so that comprehensive correlations over a range of physical properties could not be established. This shortcoming was rectified in the studies of Skelland and Lee (1981) where continuous phase mass transfer measurements were made for five different liquid-liquid systems with varying physical and transport properties. In addition, experiments were conducted using several vessel geometries. Two different vessels and two six-bladed turbine impellers of varying diameter were used. Total interfacial area during mixing was determined from photographs of the dispersion taken through the vessel wall. From a derivation based on periodically varying penetration theory and penetration theory with Kolmogoroff’s time scale, a generalised correlation was developed for the experimental data:
\[
\frac{k_c}{\sqrt{ND}} = 2.932 \times 10^{-7} \phi^{-0.508} \left( \frac{d_i}{T} \right)^{0.548} (N_{Re})^{1.371} \tag{2.23}
\]

where \( \phi \) is the dispersed phase volume fraction and definition of remaining parameters are the same as those in equation (2.22).

The authors suggested that the data could be better represented in two separate correlations for low and high interfacial tension systems rather than the general correlation shown above.

High interfacial tension systems:

\[
\frac{k_c}{\sqrt{ND}} = 2.344 \times 10^{-7} \phi^{-0.529} \left( \frac{d_i}{T} \right)^{0.701} (N_{Re})^{1.394} \tag{2.24}
\]

Low interfacial tension systems:

\[
\frac{k_c}{\sqrt{ND}} = 1.864 \times 10^{-6} \phi^{-0.287} \left( \frac{d_i}{T} \right)^{0.548} (N_{Re})^{0.095} \tag{2.25}
\]

Skelland and Moeti (1990) measured continuous phase mass transfer coefficients using experimental techniques and systems similar to the ones used by Skelland and Lee (1981). They have used several solutes which had a 7 fold increase in diffusivity as compared to those used by Skelland and Lee (1981) which only had a 1.5 fold increase in diffusivity. Using 180 mass transfer coefficient data points, the following relationship between molecular diffusivity, \( D \), and continuous phase mass transfer coefficient was established:

\[
k_c \propto D^{2/3} \tag{2.26}
\]
The exponent $2/3$ indicates that small drops were internally stagnant resembling solid spheres. On this basis, the mechanism for mass transfer could be in accordance with boundary layer theory for rigid spheres (Calderbank, 1967), eddy cell model for rigid surfaces (Lamont and Scott, 1970) and others listed in Skelland and Moeti (1990). The authors presented a general correlation for their data:

$$
\frac{k_c d_p}{D} = 1.237 \times 10^{-5} \left( \frac{\mu_c}{\rho_c D} \right)^{\frac{1}{3}} \left( \frac{d_p}{N_{Re}} \right)^{\frac{2}{3}} \left( \frac{d_p}{d_p} \right)^{2} \left( \frac{d_p}{T} \right)^{\frac{1}{2}} \left( \frac{\rho_d d_p g}{\sigma} \right)^{\frac{5}{4}} \phi^{-\frac{1}{2}}
$$

(2.27)

where $d_p =$ drop diameter, m

$g =$ acceleration due to gravity, m/s$^2$

$\sigma =$ interfacial tension, N/m

$\rho_d =$ dispersed phase density, kg/m$^3$

Remaining parameters in equation (2.27) are the same as those defined in equations (2.22) and (2.23).

Authors implied that the above correlation be safely restricted to systems with intermediate or high interfacial tensions ($\sigma \geq 0.015$ N/m) and low dispersed phase volume fractions ($\phi \leq 0.06$).

**Agitated solid-liquid systems**

Harriot (1962) developed a mass transfer correlation for suspended solid particles namely, spherical ion exchange beads. Most of the experimental work was conducted under baffled conditions with a turbine impeller. The tests covered a five fold range in tank sizes and impeller sizes, a ten fold range in stirrer speeds and a one thousand fold range is particle sizes. In addition, several combinations of ion exchange particles and continuous phase solutions were used. This allowed a good variation in density difference, viscosities and diffusivities. The effects of these variables on mass transfer coefficient were explained using slip-velocity theory along with a modified penetration theory. For conditions under which
natural convection effects are absent and when $N_{Re} > 1$, Harriot (1962) produced the following semitheoretical equation:

$$N_{sh} = \frac{k_c d_p}{D} = 2 + 0.6 \left( N_{Re} \right)^{1/2} \left( \frac{\mu_c}{\rho_c D} \right)^{1/3} \quad (2.28)$$

where $N_{sh}$ = Sherwood number

$N_{Re}$ = impeller Reynolds number ($\rho_c N d_i^2 / \mu_c$)

$D$ = diffusion coefficient, m$^2$/s

$N$ = impeller speed, rps

$d_i$ = impeller diameter, m

$k_c$ = continuous phase mass transfer coefficient, m/s

$\rho_c$ = continuous phase density, kg/m$^3$

$\mu_c$ = continuous phase viscosity, Pa.s

$d_p$ = particle diameter, m

Results in this work indicated that mass transfer coefficients for large and heavy particles in water are predicted quite well by equation (2.28). However, the slip velocity theory was found to be less than adequate in predicting coefficients for systems with low to moderate density difference, low diffusivity or cases where particle sizes are small.

Calderbank and Moo-Young (1961) examined the mass transfer properties in gas-liquid systems. Aerated mixing vessels and sive and sintered plate columns were used to produce the dispersions. Their correlations, however, have been combined with numerous other published data for heat and mass transfer in liquid-liquid and solid-gas dispersions. The authors produced the following correlation for continuous phase mass transfer in mixing vessels:

$$k_c = 0.13 \left( \frac{\rho_c \mu_c}{\rho_c^2} \right)^{1/4} \left( \frac{\mu_c}{\rho_c D} \right)^{-2/3} \quad (2.29)$$

where $k_c$ = continuous phase mass transfer coefficient, m/s

$\rho_c$ = continuous phase density, kg/m$^3$
\[ \mu_c = \text{continuous phase viscosity, Pa.s} \]
\[ D = \text{diffusion coefficient, m}^2/\text{s} \]
\[ P_v = \text{Power dissipated by the agitator per unit volume, W/m}^3 \]

The impeller dimensions are not included in the correlation and thus the equation has a simple form. Nagata (1975) argues the fact that the mass transfer coefficient is independent of particle size, may be a shortcoming of the above equation. Nevertheless, studies such as Zaldivar et al (1996) and Van Woezik and Westerterp (2000) adopted equation (2.29) to determine continuous phase mass transfer coefficient in their respective liquid-liquid systems.

Levins and Glastonbury (1972) investigated transport-controlled mass transfer to solid particles suspended in a stirred vessel. The use of several types of ion exchanges particles and liquids enabled the authors to examine the effect of physical and transport properties on the mass transfer coefficient. Variation in vessel sizes and several impeller types were also included in their experimental program. The particle size distribution and total surface area were determined by counting the particles under a microscope. The correlation developed to best describe the data was expressed as:

\[
\frac{k_L d_p}{D} = 2 + 0.47 \left( \frac{d_p^{4/3} \varepsilon^{1/3}}{\nu} \right)^{0.62} \left( \frac{d_I}{T} \right)^{0.17} \left( \frac{\nu}{D} \right)^{0.36} \quad (2.30)
\]

where

- \( k_L \) = mass transfer coefficient, m/s
- \( \varepsilon \) = energy dissipation per unit mass, W/kg
- \( \nu \) = kinematic viscosity, m\(^2\)/s
- \( T \) = vessel diameter, m
- \( d_p \) = particle diameter, m
- \( D \) = diffusivity, m\(^2\)/s
- \( d_I \) = impeller diameter, m
The exponents of diffusivity and Schmidt number \((v/D)\) suggests that mass transfer occurs predominantly by slip velocity mechanism with some contribution from steady state transfer. Variation of impeller type is factored by the use of energy dissipation per unit mass which is a function of impeller design. The effect of particle density on the mass transfer coefficient was not generally large and can be ignored with little error in many cases. However, in cases where a significant density difference exists an alternative correlation was produced by the authors.

Mass transfer coefficients for suspended particles were measured in agitated vessels and bubble columns by Sano et al (1974). Variations in vessel diameters were examined in both fully baffled and un-baffled conditions. Particle sizes ranged from 60 to 1100 µm including both spherical beads (ion exchange resin) and granules (benzoic acid, K\(\text{MnO}_4\), and β-naphthol). The results showed that the effect of equipment geometry and the method of energy supply were found to be negligible for both agitated vessels and bubble columns. Following expression was produced to describe the mass transfer coefficient for their experimental work:

\[
N_{sh} = \frac{k_L d_p}{D} = \left[ 2 + 0.4 \left( \frac{\varepsilon d_p^4}{v^1} \right)^{1/4} \left( \frac{v}{D} \right)^{1/3} \right] \phi_C \quad (2.31)
\]

Effects of particle shape were accounted for in the Carman’s shape factor, \(\phi_C\) and other parameters in equation (2.31) are the same as those defined in equation (2.30).

Asai et al (1988) examined the rates of mass transfer for fine particles less than 100 µm in diameter. Solid particles were suspended in baffled vessels of standard geometry. Most mass transfer experiments were carried out in dilute suspension by batchwise operation. Results indicated that for large particles, mass transfer coefficient, \(k_L\) varied to the 2/3 power of diffusivity which is an indication of an agreement with the theoretical prediction of mass transfer in a laminar boundary layer. These results were in agreement with Levins and Glastonbury’s (1972) correlation. On the other hand for fine particles, the mass transfer coefficient values deviated below the correlation and rapidly reached the theoretical limiting value of the Sherwood number \((N_{sh} = 2)\) which is associated with the molecular diffusion in a stagnant fluid. This leads to an argument that the mass transfer coefficient to and from very
fine particles suspended in turbulent liquids occurs by molecular diffusion rather than
turbulent diffusion. The authors produced a new correlation for their mass transfer
coefficient data:

\[
N_{Sh} = \frac{k_d d_p}{D} = \left[ 2^{5.8} + \left\{ 0.61 \left( \frac{\rho_d}{\rho} \right)^{4/3} \left( \frac{\nu}{D} \right)^{0.58} \left( \frac{\nu}{D} \right)^{1/3} \right\} \right]^{1/5.8}
\]

(2.32)

where \( 0.0229 < \frac{\nu}{D} \frac{d_p^{4/3}}{\nu} < 492 \)

\( 269 < N_{Sc} \) (Schmidt number) < 11,300

The parameters used in equation (2.32) are as defined for equation (2.30). This correlation
satisfied the notion of Sherwood number approaches the theoretical limiting value of 2 for
small particles.

### 2.1.3.1 Dispersed Phase Mass Transfer Coefficient

The dispersed mass transfer coefficient for liquid-liquid systems will depend on the
behaviour of the droplets and whether or not they are rigid (Hanson, 1971). For rigid
droplets, Treybal (1963) presented the following relationship for spheres with no circulation
and with mass transfer by pure diffusion:

\[
N_{sh_d} = \frac{2\pi^2}{3}
\]

(2.33)

where \( N_{sh_d} \) is the Sherwood number for the dispersed phase and it is defined
as \( N_{sh_d} = k_d d_{32} / D \). The dispersed phase mass transfer coefficient can be expressed as:

\[
k_d = \frac{2\pi^2 D}{3d_{32}}
\]

(2.34)

where \( D = \) diffusion coefficient, \( m^2/s \)

\( d_{32} = \) Sauter mean diameter of droplets, \( m \)
For drops with internal circulation, the mixing in the drop can be laminar or turbulent. For the regime of laminar circulation, the relation of Kronig and Brink (1960) can be used for the determination of the dispersed phase mass transfer coefficient:

\[ k_d = \frac{17.9 D}{d_{32}} \]  
\[ (2.35) \]

This correlation is restricted to regimes where drop Reynolds number, \( N_{Re,p} < 1 \). However, Johnson and Hamielec (1960) found that it can be used in some cases for higher values of \( N_{Re,p} \). For drops with turbulent circulation, the model of Handlos and Baron (1957) can be used as a good approximation (Zaldivar et al., 1996):

\[ k_d = 0.00375 u_t \left( \frac{\mu_c}{\mu_c + \mu_d} \right) \]  
\[ (2.36) \]

where \( u_t \) = droplet terminal velocity, m/s  
\( \mu_c \) = continuous phase viscosity, Pa.s  
\( \mu_d \) = dispersed phase viscosity, Pa.s

The terminal velocity of droplets in liquids with low viscosities (between 1 and 10 cP) and high interfacial tension (between 25 and 45 mN m\(^{-1}\)) can be estimated using the following correlation (Hu and Kintner, 1955):

\[ u_t = \sqrt{\frac{4gd_{32}\Delta \rho}{3\rho_cC_D}} \]  
\[ (2.37) \]

where \( d_{32} \) = Sauter mean diameter of droplets, m  
\( g \) = acceleration due to gravity, m/s\(^2\)  
\( \Delta \rho \) = density difference between dispersed and continuous phase, kg/m\(^3\)  
\( C_D \) = drag coefficient  
\( \rho_c \) = continuous phase density, kg/m\(^3\)
2.1.4 Estimation of Diffusion Coefficients in Liquids

The starting point for many correlations for diffusion coefficients in liquids is the Stokes-Einstein equation (Cussler, 1984):

\[
D_{AB} = \frac{k_B T_m}{6\pi \mu R_o}
\]  

(2.38)

where \(D_{AB}\) = diffusivity of solute A in solvent B, m²/s  
\(k_B\) = Boltzmann constant  
\(T_m\) = Temperature, °K  
\(R_o\) = Radius of solute molecule, m  
\(\mu\) = solution viscosity, Pa.s

Based on equation (2.38), Wilke and Chang (1955) obtained an equation for predicting diffusivities in dilute solutions of nonelectrolytes:

\[
D_{AB} = \frac{117.3 \times 10^{-18}(\varphi M_B)^{0.5} T_m}{\mu V_A^{0.6}}
\]  

(2.39)

Where  
\(M_B\) = molecular weight of solvent, kg/kmol  
\(V_A\) = solute molal volume at normal boiling point, m³/kmol  
\(\varphi\) = association solvent factor  
= 2.26 for water as solvent  
= 1.9 for methanol  
= 1.5 for ethanol  
= 1.2 for propanol  
= 1.0 for others
Above correlation is one of the most widely used for the estimation of diffusivities in binary liquids (Perry and Green, 1998). The correlation was the preferred choice for several investigations on reactive liquid-liquid systems (Hiraoka et al., 1990; Bourne, 2003). However there numerous other correlations available including Hayduk and Minhas (1982) which provides an accurate estimation of diffusivity for binary hydrocarbon mixtures:

\[
D_{AB} = 133 \times 10^8 T_m^{1.47} \mu^{102/V_A^{-0.79}} V_A^{0.71}
\]

(2.40)

Other empirical correlations of diffusion can be found in various literature sources (Perry and Green, 1998; Cussler, 1984; Hines and Maddox, 1985).

2.1.5 Reaction Kinetics

The system under study in the present work involves the reaction of monoethanolamine (MEA) and polysiobutylene succinic anhydride (PIBSA) to produce an emulsifier (ester and amide derivatives). The production of the emulsifier follows the reaction scheme shown below:

\[
\text{PIBSA + MEA} \rightarrow \text{PIBSA derivative emulsifier}
\]

Figure 2.8: Reaction scheme that represents the formation of the PIBSA derivative emulsifier.

In the earlier discussion on the overall reaction rate, the rate equation was based on irreversible second order reaction with the order being one respect to each of the two reactants. Assuming the same orders for the reactants in the present system, the reaction rate equation can be written as:
\[ r = kC_{\text{PIBSA}}C_{\text{MEA}} \]  

(2.41)

Where \( r \) is the reaction rate and \( C_{\text{PIBSA}} \) and \( C_{\text{MEA}} \) are the concentrations of PIBSA and MEA, respectively. The parameter \( k \) is the reaction rate constant with the unit of \( \text{m}^3/\text{mol.s} \). The emulsifier production reaction is considered to be exothermic (i.e. the reaction rate increases with increasing temperature). For such cases, the reaction rate constant, has been found to be well represented by Arrhenius law (Levenspiel, 1972). This is expressed as:

\[ k = k_0 e^{-E_A / R_g T_m} \]  

(2.42)

where \( k_0 = \) frequency or pre-exponential factor, \( \text{m}^3/\text{mol.s} \)

\( E_A = \) activation energy of the reaction, \( \text{J/mol} \)

\( R_g = \) gas constant, \( \text{J/mol} \)

\( T_m = \) reaction temperature, \( ^\circ \text{K} \)

To the authors’ best knowledge kinetics of the reaction in the present investigation is not available in open literature. In fact, kinetics data for two phase fluid reactions are usually lacking (Trambouze et al, 1988). However, there are some agitated liquid-liquid reactions which were studied extensively in the past. Alwan et al (1983) produced kinetic data for the alkaline hydrolysis of n-amyl acetate which was subsequently used by Issanchou et al (2003) for modelling the process. Similarly, D’Angelo et al (2003) was able model the nitration by mixed using the kinetics data produced by Zaldivar et al (1995; 1996). It is evident from the formulation of equation (2.6) that reaction rate constant is an important component in the overall rate expression for heterogeneous liquid-liquid reactions. Therefore knowledge of reaction kinetics is absolutely essential in the design of liquid-liquid reactors.
2.2 Interfacial Area and Drop Sizes in Agitated Dispersions

The analysis of stirred liquid-liquid dispersions requires the knowledge of interfacial area which is evaluated by the expression;

\[ a = \frac{6\phi}{d_{32}} \]  \hspace{1cm} (2.43)

where \( a \) = interfacial area, \( \text{m}^2/\text{m}^3 \)

\( \phi \) = dispersed phase volume fraction

\[ d_{32} = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2} \]  \hspace{1cm} (2.44)

The Sauter mean diameter, \( d_{32} \) cannot be evaluated through simple analysis. Therefore it is customary to evaluate the maximum stable drop diameter, \( d_{\text{max}} \) existing near the impeller and multiply it by an empirical factor to obtain \( d_{32} \) (Sprow, 1967). The \( d_{\text{max}} \) has a theoretical basis and this will be discussed in details by considering drop breakup mechanisms in both laminar and turbulent conditions. For instance, a drop in turbulent conditions is assumed to break under the influence of turbulent inertial stresses, which tend to deform it (Kumar et al, 1991). The elastic stress generated due to interfacial tension on the other hand tends to restore the drop to its original shape. As the diameter of the drop decreases, the deforming stress across it also decreases whereas the restoring stress increases. A diameter is finally reached where the deforming stress is unable to break the drop any further. This diameter is referred to as \( d_{\text{max}} \), the maximum stable drop diameter encountered in the impeller zone of the vessel.

2.2.1 Liquid-liquid Dispersions in Laminar Flow

There are practically no data or fundamental analysis for drop dispersions in stirred tanks under laminar flow conditions (Paul et al, 2004). Reasons being that viscous formulations are often produced in highly specialised equipment and exhibit complex and varied
rheological behaviour so that results are not readily generalised. Furthermore, drop size data are difficult to acquire due to limited measurement techniques and numerous handling and disposal issues. Therefore, most studies have focused on single drops in highly idealised flow fields such as simple shear and extension (Taylor, 1932, 1934; Karam and Bellenger, 1968; Rumscheidt and Mason, 1961; Grace, 1982; Bentley and Leal, 1986). These studies have led to a better understanding of drop dispersions in laminar flow conditions and formed a basis for process design and scale-up.

### 2.2.1.1 Single Drop Breakup in Laminar Conditions

In order to predict the size of drops, the concept of critical or maximum stable drop size, \( d_{\text{max}} \), is of central importance. It is defined as the size above which a parent drop will become unstable and break up into smaller drops. It has been shown that \( d_{\text{max}} \) in laminar flow can be calculated from the critical capillary number, \( C_{a_{\text{cr}}} \) (Pacek et al., 2001).

\[
C_{a_{\text{cr}}} = \frac{\tau}{\sigma/R_{\text{max}}} \tag{2.45}
\]

where

\( \tau = \) shear stress, N/m\(^2\)
\( \sigma = \) interfacial tension, N/m
\( R_{\text{max}} = \) maximum stable drop radius, m

According to Taylor (1932), droplet breakup in laminar shear flow is governed by the viscous shear stress \( \tau = \mu_c \dot{\gamma} \), where \( \dot{\gamma} \) is the shear rate and \( \mu_c \) is the continuous phase viscosity. Thus the critical capillary number can take the form:

\[
C_{a_{\text{cr}}} = \frac{\mu_c \dot{\gamma} d_{\text{max}}}{2\sigma} \tag{2.46}
\]

The capillary number is the ratio of viscous forces acting to deform the drop to the surface force opposing deformation (Paul et al., 2004). The number is a function of the ratio of dispersed and continuous phase viscosities and on the type of flow (Pacek et al., 2001).
Figure 2.9 shows the critical stability for Newtonian fluids in simple shear flow and simple extensional flow. A drop at conditions above the curve is unstable and will break. The drop is stable at conditions below the curve.

![Critical Stability Curve](image)

**Figure 2.9: Critical stability curve for simple shear and simple extensional flow (Paul et al., 2004).**

Taylor (1934) was one of the first to investigate the drop breakage in shear flow. As a result of his experimental and theoretical work, he established an analytical relationship between the degree of deformation and the deformation rate.

\[
D_c = \frac{L_d - B_d}{L_d + B_d} = \frac{G \rho \mu_c}{2 \sigma} \left( \frac{19/16 (\mu_d/\mu_c) + 1}{(\mu_d/\mu_c) + 1} \right) = Ca \cdot f (\mu_d/\mu_c)
\]  \hspace{1cm} (2.47)

The deformation is defined by \((L_d - B_d)/(L_d + B_d)\) where \(L_d\) is the length and \(B_d\) is the width of the deformed drop. When the viscosity ratio, \(\lambda = \mu_d/\mu_c\) reaches a critical value, the drop breaks up in two parts (Jegat et al., 1998). Karam and Bellenger (1968) experimentally determined single drop break up as a function of viscosity ratio. Studies of single drop deformation in simple shear flow were also examined by Grace (1982). The conditions for breakage were observed within a glass-walled Couette apparatus consisting of independently
controlled, counter rotating concentric glass cylinders. Bentley and Leal (1986) studied
deformation and breakup of drop in four-roll mill that allowed specification of idealised flow
with various degrees of shear and extension. They plotted critical capillary number versus
viscosity ratio of their data, but also those of Taylor (1934), Rumscheidt and Mason (1961)
and Grace (1982). The graph shown in Figure 2.11 is an example of this.

Following Grace’s study on droplet break up in simple shear flow, it is reported that the
droplet breakup can occur at viscosity ratio more favourably in the range of \( \lambda = 0.1-1 \)
corresponding to a minimal value \( C_{a_{cr}} \approx 1 \) (Schubert and Armbruster, 1992). For lower
values of \( \lambda \) (i.e 0.01), a very high shear rate \( (\dot{\gamma} \approx 10^6-10^7 \text{ s}^{-1}) \) is required to obtain small
droplets \( (d_p < 1 \mu m) \) (Walstra, 1993). One the other hand, for higher values of \( \lambda \), the shear
strain is less efficient to break up droplets. As such the droplets behave like rigid spheres. If
the viscosity ratio \( \lambda \geq 4 \), no drop division can occur however large the shear rate is (Grace,
1982; Janssen and Meijer, 1993). The former analysis is also valid for the extensional
laminar flows, in which the extension rate \( \varepsilon \) is included in the definition of critical capillary
number: \( Ca_{cr} = \mu \dot{\gamma} \varepsilon_{max} / 4\sigma \). In elongation flow, \( C_{a_{cr}} \) is less dependent on \( \lambda \) and for \( 10^{-3} \leq \lambda \leq 10^3 \), \( C_{a_{cr}} \) lies between 1 and 0.1. Furthermore when \( \lambda \) is about 1, the \( C_{a_{cr}} \) is close to 0.3
suggesting better efficiency of the extensional flow at same rate (Lemenand et al, 2003). In
this type flow, burst of droplet is not limited by viscosity ratio; drops can be broken
regardless of the \( \lambda \) (Janssen and Meijer, 1993). In the absence of data for practical flows,
single drop break up information in idealised studies has been utilised to develop model for
drop breakage in laminar flows such as the boundary layer shear breakup model.

### 2.2.1.2 Boundary Layer Shear Breakup

There is a boundary layer on the impeller blade itself and a drop present in it can experience
strong shearing action leading to its breakage provided the drop diameter is smaller than the
boundary layer thickness (Kumar et al, 1991). Schematic of the shear break up in the
boundary layer mechanism is shown Figure 2.10. This mechanism has been examined by
Leng and Quarderer (1982), Cherry and Papoutsakis (1986), Kumar et al (1991), and
Kumar et al (1991) suggested that the drop passing through the boundary layer may experience different shear rates depending on its position. In their analysis average shear rate was calculated and drops were assumed to break under average values. This lead to an expression for $d_{\text{max}}$, the maximum drop size under the shear flow condition (Kumar et al, 1991):

$$d_{\text{max}} = \frac{Ca_{cr} \sigma}{113.2 N^{1.2} \mu^{0.8}} \left( \frac{1}{L^3 \rho} \right)^{0.2}$$  \hspace{1cm} (2.48)

where $Ca_{cr} = \text{critical capillary number}$

- $N = \text{impeller speed, rps}$
- $\rho = \text{density, kg/m}^3$
- $\mu = \text{viscosity, N.s/m}^2$
- $L = \text{impeller blade length, m}$
- $\sigma = \text{interfacial tension, N/m}$

The expression was modified with new estimates of velocity at the tip (Kumar et al, 1998):

$$d_{\text{max}} = \frac{Ca_{cr} (\lambda) \sigma}{15.4 N^{1.2} \mu^{0.8}} \left( \frac{\mu}{L^3 \rho} \right)^{0.2}$$  \hspace{1cm} (2.49)
For the proposed mechanism and the $d_{\text{max}}$ equation to be applicable, the drop diameter should be smaller than the boundary layer thickness. Kumar et al (1991) found that the boundary layer was 2 to 8 times the value of $d_{\text{max}}$. In their analysis, the dispersion was treated as a single fluid and the drop being analysed was also a part of the emulsion so that it was contributing to the overall rheology. It was explicitly assumed that, during the breakage, a drop experiences the average viscosity of the emulsion and not the viscosity of just the continuous phase. Thus the drop-drop interaction was incorporated in the effective viscosity itself. Variation of critical capillary number in shear flow, $C_{\text{as}}$ with $\lambda$ used by Kumar et al (1991) is shown in Figure 2.11.

\[ C_{\text{as}} = \frac{\rho d_{\text{max}} \mu_c}{2\sigma} \]
\[ \lambda = \frac{\mu_d}{\mu_c} \]

![Figure 2.11: $C_{\text{as}}$ vs $\lambda$](image)

Figure 2.11 shows that as $\lambda$ increases beyond the value of 1, drop break up becomes increasingly difficult and for $\lambda > 3$, the shear flow field fails to breakup drops as $C_{\text{as}}$ approaches infinity.
Leng and Quarderer (1982) reasoned that dispersion occurred in the boundary layer adjacent to the impeller surfaces and that the impeller vertical elements could be approximated by cylinders moving through the suspension at the relative impeller tip speed. For conditions under which laminar shear forces dominate, the following expression for $d_{\text{max}}$ was obtained:

$$d_{\text{max}} = \text{Const.} \left[ \frac{D_c}{\mu_c \rho_c} \right]^{1/2} \left[ \frac{1}{Nd_t} \right]^{1/2} \left[ \frac{1}{1 - k_v} \right] \left[ \frac{1}{1 + \frac{\mu_d}{\mu_c}} \right] \left[ \frac{\mu_d}{\mu_c} \right] \phi \left( \frac{\mu_d}{\mu_c} \right)$$  (2.50)

The parameter $D_c$ is the diameter of the cylinder and $k_v$ is the ratio of the local tangential velocity to the impeller tip speed. The ratio depends on the degree of baffling and position in the tank but is independent of the Reynolds Number and scale of geometrically similar vessels, provided $N_{Re} > 10^4$. Using paddle impeller, Aiba (1958) showed $k_v$ to be 0.30 for un-baffled and 0.60 for baffled vessels at the impeller tip.

Pacek et al (2001) examined aqueous/aqueous drop breakage in laminar to low transitional regime. They understood that local shear rate data was not readily available, hence they used the well established average shear rate concepts developed by Metzner and Otto (1957):

$$\dot{\gamma} = k_v N$$  \hspace{1cm} (2.51)

The shear rate constant, $k_v$, is derived from power measurement taken in the laminar regime and is only a function of impeller type (Harnby et al, 1992). Using equation (2.46) for drop breakage in laminar conditions and equation (2.51), Pacek et al (2001) produced the following correlation for establishing maximum stable drop diameter:

$$Ca_{et} = \frac{[d_{\text{max}}/2] k_v N \mu_c}{\sigma}$$  \hspace{1cm} (2.52)

Using the assumption that drop size in agitated vessels is comparable with the laminar boundary layer thickness at the impeller blades, Wichterle (1995) produced correlations to predict terminal drop size, $d_p$:  

51
Their correlations were found to fit data sets from numerous published literatures (Sprow, 1967; Brown and Pitt, 1970; Mlynik and Resnick, 1972; Konno et al, 1977; Stamotoudis and Tavlarides, 1985; Calabrese et al, 1986a; Collias and Prud’homme, 1991; Collias and Prud’homme, 1992) fairly well. Given the scatter of the drop size data, the authors did not have a preferred equation. In any case, both correlations suggest that the viscosity ratio is insignificant when the dispersed phase is less viscous while it should be taken into account for viscous drops (Wichterle, 1995).

Shimizu et al (1999) suggested that models proposed by above mentioned investigators were incomplete and limited only to Newtonian continuous phase systems. Therefore they produced a new model for drop breakage in non-Newtonian continuous phase systems. In order to take into account the non-Newtonian flow behaviour, \( \mu \) was replaced by apparent viscosity, \( \mu_{\text{app}} \).

\[
\mu_{\text{app}} = K \left( k_p N \right)^{n-1}
\]  

(2.55)

where \( K = \text{consistency index in a power law model, Pa.s}^n \)

\( k_p = \text{proportionality constant} \)

\( n = \text{power law index} \)

The model developed by Shimizu et al (1999) predicts that the maximum drop diameter increases with increasing shear thinning or decreasing flow in the laminar region. With increasing shear thinning, the shear stress tending to deform the drop decreases and as a result, the maximum drop diameter increases.
2.2.2 Liquid-liquid Dispersions in Turbulent Flow

In contrast to laminar flow, there are numerous studies of drop dispersions in turbulent flow particularly for dilute systems, where coalescence can be neglected (Paul et al, 2004). To estimate the drop sizes, it is essential to know the breakup mechanism of a drop in turbulent dispersions.

Most widely accepted mechanistic models for maximum stable drop size in turbulent flow are based on the argument put forth by Kolmogoroff (1949) and Hinze (1955). Hinze (1955) suggested a model for predicting $d_{\text{max}}$ by comparing the restoring elastic stress in the drop due to interfacial tension with the inertial stress across the drop diameter. He proposed that breakup of a drop occurs when the ratio of the inertial stress to elastic stress, $\frac{\rho u^2 (\bar{d}) d}{\sigma}$, exceeds a critical value. Assuming that turbulence is isotropic and that the drop diameter $d > 1$ (Kolmogoroff length), the mean square velocity fluctuation across the distance, $\bar{d}$ is given by (Lagisetty et al, 1986):

$$u^2 (\bar{d}) \propto (\varepsilon d)^{2/3} \quad (2.56)$$

For a vessel agitated by turbine impellers or propellers operating in the constant power number regime (at high Reynolds Numbers), the power dissipation per unit mass, $\varepsilon$, can be expressed as (Wichterle, 1995):

$$\varepsilon \propto N^3 d_i^2 \quad (2.57)$$

where $N = \text{impeller speed, rps}$

$$d_i = \text{impeller diameter, m}$$

Substituting equations (2.56) and (2.57) in Hinze’s proposed criterion, Shinnar (1961) derived the following equation for the maximum stable drop diameter:

$$\frac{d_{\text{max}}}{d_i} = \text{const} \tan t(We)^{-0.6} \quad (2.58)$$
where the Weber number, 

$$\text{We} = \frac{\rho d_i N^2 d_i^3}{\sigma}$$  \hspace{1cm} (2.59)  

Equation (2.58) is valid for dilute dispersion where coalescence can be neglected. The application of this model to ‘non-coalesced’ systems was tested over a wide range of processes involving stirred vessel, emulsifiers with ultrasound and homogenisers. Many authors reported good prediction of maximum droplet diameter despite some discrepancies in the value of the constant (Lemenand et al., 2003). The constant depends on the geometry of the vessel and ranges between 0.09 and 0.15. Equation (2.58) is based on the assumption that there is minimal difference in densities and viscosities of the two phases. It cannot be used when the dispersed phase is viscous or rheologically complex as the rate deformation has not been taken into account in its development (Kumar et al., 1991). The viscosity of the dispersed phase has however been found to have significant influence on \(d_{\text{max}}\) (Arai et al., 1977; Konno et al., 1982; Lagisetty et al., 1986). The viscous stress resists the flow inside the drop as it deforms, and therefore has a significant influence on \(d_{\text{max}}\). Various models have been developed taking into account the effect of the dispersed phase viscosity on the maximum stable drop size (Lagisetty et al., 1986; Calabrese et al., 1986a; Nishikawa et al., 1987; Ohtake et al., 1987; Kuriyama et al., 1996)

Calabrese et al (1986a) used a corrective term to take viscosity of the dispersed phase into account and produced a number of correlations for dilute dispersions in agitated tanks. The following equation was proposed for low to moderate dispersed phase viscosity.

$$\frac{d_{\text{max}}}{d_i} = C_3 \text{We}^{-3/5} \left[ 1 + C_4 V_i \left( \frac{d_{\text{max}}}{d_i} \right)^{1/3} \right]^{3/5}$$  \hspace{1cm} (2.60)  

where \(V_i\) is the tank viscosity group number representing the ratio of dispersed phase viscous force to surface tension forces:

$$V_i = \frac{\mu_d N d_i}{\sigma} \left( \frac{\mu_c}{\mu_d} \right)^{1/2}$$  \hspace{1cm} (2.61)
Lagisetty *et al.* (1986) produced the following model to include the effect of the dispersed phase viscosity on $d_{\text{max}}$:

$$
\frac{4}{4C_3We\left(\frac{d_{\text{max}}}{d_i}\right)^{5/3}} \tan^{-1} \left[ \frac{1}{4C_6We\left(\frac{d_{\text{max}}}{d_i}\right)^{5/3}} - 1 \right]^{1/2} = \left( \frac{N_{Re}}{We} \right) \left( \frac{d_{\text{max}}}{d_i} \right)^{-1/3}
$$

(2.62)

The model could only be used to predict the drop size of Newtonian fluids. It was found that the effect of the dispersed phase viscosity on $d_{\text{max}}$ becomes significant only after about 20 cP. The model predicts that as $\mu_d \to 0$, it is reduced to the model represented in equation (2.58).

Measurements by Arai *et al.* (1977) and Wang and Calabrese (1986) showed that the dispersed phase viscosity has negligible influence for systems with viscosity ratio $\mu_d/\mu_c < 20$.

The models discussed thus far can predict $d_{\text{max}}$ values only when the dispersed phase volume fraction is very low ($\phi < 0.05$).

### 2.2.2.1 Effect of dispersed phase volume fraction on $d_{32}$

As volume fraction is increased the drop size has generally been found to increase (Kumar *et al.*, 1991). The presence of a greater amount of dispersed phase affects the equilibrium drop size in two ways. When drops are in close proximity, the small-scale structure of the continuous phase is altered, thereby decreasing the turbulent energy acting to disrupt the drop (Calabrese *et al.*, 1986b). Furthermore, higher dispersed phase volume fractions also leads to a growing collision rate of drops resulting in an increasing number of breakage and coalescence processes. Given that the coalescence process requires the collision between drops and the number of collisions between drops is greater with increased dispersed phase fraction, the increase in coalescence rate is more pronounced than the breakage rate. Both effects lead to an increase in $d_{32}$. Doulah (1975) and Brown and Pitt (1972) however believed that, given that the drop sizes in the vicinity of the impeller has been shown to be determined by break-up mechanism, the effect of $\phi$ on $d_{32}$ is due to the damping effect of the dispersion on turbulence and not due to coalescence.
The effect of $\phi$ on $d_{32}$ has been taken into account by introducing a semi-empirical modification in equation (2.58). Various expressions used by different investigators to calculate $d_{\text{max}}$ have been reviewed by Coulaloglou and Tavlarides (1976). The general form of the correlation is:

$$\frac{d_{\text{max}}}{d_i} = C_7 (1 + C_8 \phi) We^{-0.6} \quad (2.63)$$

The constant $C_7$ depends on the impeller type whereas $C_8$ is a measure of the tendency to coalesce (Kraume et al, 2004). Systems that coalesce easily have high values of $C_8$ and those that coalesce slowly have low ones. Values of the constant $C_8$ are generally in the range of 3-10 depending on the nature coalescent system (Lemenand et al, 2003). In stirred vessels, Pacek et al (1998) have found that $C_8 = 22.8$. The authors attributed this very large value to the highly coalescent system used in their study (chlorobenzene/water). Lagisetty et al (1986) obtained the following expression for dispersed phase with low viscosity:

$$\frac{d_{\text{max}}}{d_i} = C_9 (1 + C_{10} \phi)^{6/5} We^{-3/5} \quad (2.64)$$

When $C_{10} = 4$, predictions of this model were found to be close to the experimental data of Coulaloglou and Tavlarides (1976). Equations (2.63) and (2.64) predict that as $\phi$ increases the $d_{\text{max}}$ value should increase monotonically. However, at higher dispersed phase volume fractions (about $\phi > 0.4$) the experimental results are absolutely contrary to general trend predicted. Not only do they not follow these equations, but the $d_{\text{max}}$ values decrease with increasing $\phi$. As the normal breakage mechanisms (based on eddy drop interaction) usually employed to describe breakage in stirred vessels cannot explain this unusual behaviour, Kumar et al (1991, 1998) provide an alternative mechanisms of drop breakage. These mechanisms involve elongation flow breakage layer at the impeller flow along the impeller length and the shear mechanism operating in the boundary layer at the impeller.
2.2.2.2 Minimum Stable Drop Diameter

Shinnar (1961) derived an equation for the minimum drop diameter, $d_{\text{min}}$, resulting from turbulent fluctuations and adhesion forces. Thereby, the effect of coalescence is taken into account. $D_{\text{min}}$ is defined as the minimum diameter of a drop which is stable against coalescence in a turbulent dispersion and can be expressed as (Shinnar, 1961):

$$d_{\text{min}} = C_{11} \varepsilon^{-1/4} \rho_c^{-3/8} A(h_o)$$

(2.65)

Where $A(h_o)$ is the energy necessary to completely separate two drops with unit diameter, which are initially separated by a distance, $h_o$ and is determined by the properties of the liquids. Sprow (1967) derived a similar expression. More recently, Liu and Li (1999) proposed the following expression for determining $d_{\text{min}}$:

$$d_{\text{min}} = \frac{\gamma^{1.38} \rho_c^{0.46}}{0.0272 \mu_c \rho_c^{0.84} \varepsilon^{0.89}}$$

(2.66)

According to the above relationship, the minimum stable drop diameter can be predicted directly as a function of physical properties of fluids and energy dissipation, $\varepsilon$. In coalescing regions in a stirred tank, the Sauter mean drop diameter, $d_{32}$ is directly proportional to $d_{\text{min}}$ (Liu and Li, 1999). Based on this assumption, Shinnar (1961) produced the following expression for predicting $d_{32}$ in systems dominated by coalescence:

$$\frac{d_{32}}{d_I} = C_{12} (We)^{-0.375}$$

(2.67)

Based on the experimental results and theory, most drop size correlations are expressed in terms of Weber number to the power -0.6. The exponent derived in Shinnar (1961) investigation is significantly smaller. Others have produced similar exponents, -0.4 (Laso et al, 1987) -0.36 (Roger et al, 1956) and -0.3 (Weinstein and Treybal, 1973). On the other hand, experimental results for a dilute system from Baldyga and Bourne (1993) led to an exponent of -0.9.
2.2.3 Relationship between $d_{\text{max}}$ and $d_{32}$

Maximum stable drop diameter, $d_{\text{max}}$ is determined by the balance between the deforming and restoring forces acting in the flow. Directly relating Sauter mean diameter, $d_{32}$ to fluid properties, operating conditions and tank geometry through a force or energy analysis (as was done for $d_{\text{max}}$) involve many uncertainties (Zhou and Kresta, 1998a). Nevertheless there is considerable evidence to suggest that $d_{\text{max}}$ is proportional to $d_{32}$. Sprow (1967) was first to assume that $d_{32} = C d_{\text{max}}$, and then verified this relationship with his experimental data. His assumption was confirmed by many subsequent investigations. Table 2.1 summarises some values of ‘$C$’ obtained by some investigations.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Value of $C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sprow (1967)</td>
<td>0.380</td>
</tr>
<tr>
<td>Brown and Pitt (1972)</td>
<td>0.70</td>
</tr>
<tr>
<td>Coulaloglou and Tavlarides (1976)</td>
<td>0.67</td>
</tr>
<tr>
<td>Calabrese et al (1986b)</td>
<td>0.48-0.60</td>
</tr>
<tr>
<td>Nishikawa et al (1987)</td>
<td>0.5 (breakup region)</td>
</tr>
<tr>
<td></td>
<td>0.45 (coalescence region)</td>
</tr>
<tr>
<td>Berkman and Calabrese (1988)</td>
<td>0.67</td>
</tr>
<tr>
<td>Kuriyama et al (1996)</td>
<td>0.63</td>
</tr>
<tr>
<td>Zhou and Kresta (1998a)</td>
<td>0.42-0.69</td>
</tr>
</tbody>
</table>

The cases listed in Table 2.1 include batch and continuous processes, breakup and coalescence regions, various operating conditions and fluid properties. This suggests that the mean drop diameter would be always proportional to the maximum drop diameter irrespective of the difference in those conditions within which experiments were conducted. Based on the relationship ($d_{32} = C d_{\text{max}}$), many investigator have related the Sauter mean drop diameter to the physical properties of fluids in dispersions and operating conditions in agitated tanks. Some of these correlations are summarised in a number of literature sources (Coulaloglou and Tavlarides, 1976; Godfrey et al, 1989; Zhou and Kresta, 1998a; Paul et al, 2004).
2.2.4 Evolution of Drop Size Distribution

Most drop size studies have focused on the effect of physical properties of the systems or geometrical and operating conditions on steady state drop size or maximum stable drop size. In actual industrial processes, there are many cases where the operation is finished before the drop dispersion reaches a steady state, and hence the information concerning the time variation of drop size after the agitation starts is invaluable (Kuriyama et al., 1996). The process of drop breakage and coalescence essentially determine the evolution of drop size distributions in such dispersions. Some investigators have developed models to predict the evolution of drop size for agitated liquid-liquid dispersions using either drop population balances (Valentas et al., 1966; Wright and Ramkrishna, 1994; Tsouris and Tavlarides, 1994) or simulation techniques (Coulaloglou and Tavlarides, 1977; Skelland and Kanel, 1992). These models were able to determine the change in drop sizes using mathematical functions of the breakage and coalescence processes. Breakage rates are functions of breakage frequency, number of daughter drops, and breakage distribution function, which in turn are functions of the type and size of the impeller, tank diameter, the dispersed phase volume fraction and physical properties of the liquids (Hong and Lee, 1985). The drop coalescence rate has been described by Coulaloglou and Tavlarides (1977) as a function of the collision frequency and the coalescence efficiency (defined as the probability of coalescence per collision). Numerical solution of these function are highly complex and producing such solutions using data produced in the present investigation would be beyond the scope of this project. However, the results produced by these models give useful insight into transient behaviour of Sauter mean drop size at various operating conditions. A typical plot of the change in drop size with respect time is shown in Figure 2.12.
It is evident from Figure 2.12 that the Sauter mean diameter decreases exponentially during the initial period of agitation, where a large drop break up into small ones until it reaches a constant or steady state drop size. The initial decrease in decrease in drop size shows that the breakage rate exceeds the coalescence rate during the initial period of agitation. If the dispersion is maintained by agitation for a sufficiently long time, dynamic equilibrium between coalescence and breakage will be established. Under this condition, the steady state mean drop diameter can be observed (Liu and Li, 1999). The time required to reach this steady state value varies with physical properties and operating conditions of the dispersion. For instance when the drop viscosity is relatively low, steady state is reached in about an hour. On the other hand in the case of high-viscosity drops, the drop size reduces even after a lapse of one hour (Kuriyama et al, 1996). Yang et al (2000) observed the change in drop size values for approximately 150 min. Longer time of 4 hours was obtained by Apostoliduo and Stamatoudis (1991). On the other hand, Hong and Lee (1985) measured the time to reach equilibrium as less than 10 min for $0.05 < \phi < 0.2$.

Hong and Lee (1985) produced a correlation to predict the transitional behaviour of mean drop size for three liquid-liquid systems:
\[
\frac{d_{32} - d_{32}^*}{d_{32}^*} = 29.70 \left( \frac{d_f}{T} \right)^{2.015} \left( \frac{We}{N_{Re}} \right)^{0.5508} (Nt)^{0.70}
\]  
\[(2.68)\]

\(d_{32}^*\) is the predicted steady state Sauter mean diameter based on the correlation:

\[
\frac{d_{32}^*}{d_f} = 0.05(1 + 2.316\phi)\left( \frac{d_I}{T} \right)^{-0.75} N_{Fr}^{-0.13} We^{-0.6}
\]  
\[(2.69)\]

where
- \(d_{32}\) = Sauter mean drop diameter, m
- \(N\) = impeller speed, rpm
- \(d_I\) = impeller diameter, m
- \(T\) = vessel diameter, m
- \(\phi\) = dispersed phase volume fraction
- \(N_{Fr}\) = Froude number
- \(We\) = Weber number
- \(N_{Re}\) = Reynolds number
- \(t\) = time, min

Hong and Lee (1985) believed that the above correlation was an improvement to previous correlations such as Coulalogluo and Tavlarides (1976). It includes additional variables such as the Froude number defined by \((\rho c N^2 d_I^2 / \Delta \rho Hg)\) and was found to best predict the \(d_{32}^*\) for five liquid-liquid systems used in their study.

Calabrese et al (1992) produced the following correlation for the time variant \(d_{32}\):

\[
\frac{d_{32}}{d_{32}^*} = \left[ \frac{2.1 \times 10^4}{(Nt - 50) + 5.1} \right]^{\frac{1}{6}}
\]  
\[(2.70)\]

The equilibrium Sauter mean drop diameter, \(d_{32}^*\) was given by correlations presented by Calabrese et al (1986b). The monotonic decrease of drop sizes before levelling off to a final size is typically the case for batch mixers.
2.2.4.1 Drop Breakage and Coalescence Rate

Narsimhan et al (1980) measured the transient drop size distribution in a stirred liquid-liquid dispersion with a low dispersed phase volume fraction ($\phi < 0.005$) and found that the transition probability function for droplet breakage shows a steeper decline as drop size decreases towards a maximum stable value. Various correlations involving $d_{\text{max}}$ (and steady state $d_{32}$ or rather $d_{32}^*$) along with possible breakage mechanisms have been presented in earlier discussions. However, knowledge of $d_{\text{max}}$ does not give information on the dynamics of the drop breakage (Sathyagal et al, 1996). Models for breakage rates have been investigated by various authors including Coulaloglou and Tavlarides (1977); Narsimhan et al (1980); Nambier et al (1994); Tsouris and Tavlarides (1994) and Sathyagal et al, (1996).

The inverse problem approach proposed by Sathyagal et al, (1996) suggests that the breakage rate is a strong function of drop size and stirrer speed, increasing sharply with both variables. Results showed that for a small increase in interfacial tension, the breakage rate decreases very sharply. Furthermore, the breakage rate was found to decrease with increasing dispersed phase viscosity though not as sharply as with interfacial tension.

In a turbulent dispersion, drops are randomly moving about and continually colliding with each other. For coalescence to occur, the intervening liquid between collided drops has to drain to the film rupture thickness so that agglomeration can occur (Das et al, 1987). In addition, during drainage the turbulent fluctuations could separate the drops therefore would not result in coalescence. So, the coalescence efficiency is dependent on the collision efficiency. Coalescence frequency can be described as the product of collision frequency and coalescence efficiency. Several investigators have proposed models on coalescence frequency between drops in stirred dispersion (Coulaloglou and Tavlarides, 1977; Das et al, 1987; Tsouris and Tavlarides, 1994; Wright and Ramkrishna, 1994; Maggioris et al, 2000). Coulaloglou and Tavlarides (1977) have calculated the rate of collision between drops assuming that the mechanism of collision is similar to that between gas molecules as in the kinetics theory of gases. Das et al (1987) introduced a white-noise model which considers the film drainage between colliding drops as a stochastic process driven by an idealised random process for the fluctuation forces applied on the drop pair.
Quantification of coalescence rates by determining functions of collision frequency and efficiency as proposed by these models is beyond the scope of this thesis. However, it is useful to have an understanding of how various factors such as dispersed phase volume fraction, impeller speed and physical properties of the system affect collision frequency and coalescence efficiency, and ultimately the coalescence rate. Greater the dispersed phase volume fraction and hence the number density of drops, the greater the likelihood that a selected drop will encounter and collide with another drop (Yeo et al., 2002). Thus it can be stated that the collision frequency increases with increasing volume fraction. Collision frequency has also been found to increase with increases in drop size (Park and Blair, 1975; Paul et al., 2004) and increases agitation rate (Paul et al., 2004).

It has been reported in literature that in liquid-liquid dispersions, coalescence increases with an increase in viscosity of the continuous phase (Maggioris et al., 2000). Liu and Li (1999) adds that when $\mu_d/\mu_c$ is small, the interfacial mobility is large so that drops coalesce more rapidly (or higher coalescence efficiency is experienced by the system). This notion is supported by model developed by Das et al. (1987), which predicts higher coalescence efficiency for higher continuous phase viscosity. In addition increase in agitation speed was observed to reduce the coalescence efficiency. Also the coalescence efficiency was found to increase with increases in dispersed phase volume fraction (Liu and Li, 1999).
2.3 Drop Size Measurement

There are numerous measurement techniques that have been developed and used for drop size investigations. These techniques can be classified as direct photographic methods and indirect methods. Light transmittance, light scattering, chemical reaction, coulter counter, acoustic wave and scintillation are only some examples of indirect methods of drop size determination. Photographic methods include techniques such as photography through the vessel wall, photographic probe and microscopic photography. Following sections will detail some aspects of measurement techniques that have been used in previous drop size studies.

2.3.1 Indirect Methods

2.3.1.1 Light Transmittance

When a parallel beam of light passes through a dispersion, light is attenuated by the particles of the dispersed phase by reflection, refraction and diffraction. Measurement of the transmitted light allows the calculation of interfacial area per volume and from the volume fraction of the dispersed phase, Sauter mean drop size, $d_{32}$, can be calculated. Based on these principles, Vermeulen et al (1955), Roger et al (1956) and Calderbank (1958) were some of the first to develop a light transmittance technique to determine drop sizes in dispersions. Light transmittance technique was also used in a number of subsequent investigations, such as those by McLaughin and Rushton, (1973) and Eckert et al, (1985). In these studies, a light probe was immersed in a suspension or dispersion and the light transmitted in the system was used to calculate particles sizes. The method did not have any requirements of the refractive index of the dispersed phase; it may be transparent or opaque, gas, liquid or solid. Light transmittance can give immediate results, but it is sensitive to changes in volume fraction. The volume fraction must be a known quantity as the transmittance and absorption of light depends not only on the sizes of drops, but also upon the volume fraction of the dispersed phase (Smith, 1973). The presence of air bubbles in the system is undesirable, as they interfere with the light transmission technique for measuring interfacial area (Eckert et al, 1985). Therefore the technique is unsuitable for systems where likelihood of air bubble entrapment is high. In addition, drops of diameter less than 0.1 mm can scatter light and cause inaccuracy in determining interfacial area by the method.
Chapter 2

2.3.1.2 Light Scattering

Zhou and Kreta (1998b) developed a technique which is based on the difference in refractive index of the dispersed and continuous phase called phase Doppler particle analyser (PDPA). The PDPA measures the phase difference in the scattered light between two collection angles and uses this phase difference to determine the diameter of drops. Wille et al (2001) adopted a similar technique to examine the effect of impeller types on drop sizes. One limitation of the techniques is that both phases in the system must be transparent and to obtain good results, the refractive indices of the phase must also be quite different. In addition, Phase Doppler anemometry (PDA) techniques such as those mentioned above are only useful for very low dispersed phase concentrations (Paul et al, 2004). An advantage of the technique is that all instrumentation is placed outside the vessel eliminating the disturbance to the hydrodynamics of the system.

2.3.1.3 Coulter Counter

Sprow (1967) obtained drop size distributions emulsions using a Coulter counter. This instrument determines the size of drops suspended in an electrically conductive continuous phase by forcing the emulsion through a small aperture between electrodes. The resistance between the electrodes changes as a particle goes through the aperture is measured and this change is converted to a voltage pulse. Given that these pulses are proportional to drop volume, the drop diameter corresponding to a particular particle count can be determined. Narsimhan et al (1980) also used the Coulter counter technique to determine drop sizes in a drop breakage study of lean liquid-liquid dispersions. It should be noted that in order to take full advantage of the electronic counting methods, the continuous phase must be moderately conductive. This limits the number of systems that can be studied using the Coulter counter method. The technique required the addition of undesirable conductive materials to the dispersion. It is difficult to predict how these materials would affect the drop diameter and the breakage and coalescence rates in dispersions (Bae and Tavlarides, 1989).
2.3.1.4 Capillary Technique

Capillary techniques employ a fine capillary bore of the order of the droplet sizes for sampling from the liquid dispersion. The basic principle is to force representative sample through the capillary by developing a pressure difference across the tube. As drop passes through the capillary, they are transformed to cylindrical slugs of equivalent volume. Based on the difference in either conductivity or light absorption, the length of the slug and drop size is calculated. Bea and Tavlarides (1989) and Weiss et al (1997) employed an optical device to measure drop size by the difference in light absorption. The technique is limited by the necessity of sufficient difference of light refraction for drop size measurement and sufficient light absorbance of the solute in the drop for concentration measurement. A capillary technique based on electrical conductivity to measure drop size and concentration was developed by Hocq et al (1994). The technique is able to produce rapid and effective results especially useful in monitoring reactive liquid-liquid dispersions. However, it was confined to systems that were electrically conductive and the technique was able to measure drop sizes accurately for drops above 1.0 mm in diameter. Main disadvantage of the capillary technique is the choice of capillary diameter limits the size of smallest drop which can be accurately detected. Detailed description of the limitation of the capillary technique is detailed in Pacek and Nienow (1995).

2.3.1.5 Chemical Method

Chemical method was developed by Westerterp et al. (1963) to evaluate the interfacial area in a gas-liquid system, but several subsequent studies has adapted the technique for liquid-liquid systems (Nanda and Sharma, 1966; Fernandes and Sharma, 1967; Alwan et al, 1983; Zaldivar et al, 1996 and van Woezik and Westerterp, 2000). Chemical method enables interfacial area to be quantified through the mass transfer between phases or an accompanying chemical reaction. Chemical method is advantageous because it determines the so termed global interfacial area, whereas physical methods (which constitute all other drop size measurement techniques) only provide local values in the heterogeneous system. Generally, chemical methods tend to have a bias toward smaller size distribution. These may be missed by physical methods. Thus the results from chemical and physical methods do not agree (Paul et al, 2004). Primary disadvantage of the chemical method is that the effect of
mass transfer on the physiochemical properties of the dispersion is neglected. Some investigators such as Zaldavar et al (1996) determined the drop size distribution assuming that the physiochemical properties of the system remain constant. However, it has been observed that mass transfer can affect the interfacial tension and thus interfacial area (Bae and Tavlarides, 1989).

2.3.1.6 Other Indirect Methods

Smith et al (1974) devised acoustic wave method for the simultaneous determination of volume fraction and drop sizes. It was developed using the difference in elastic properties of the continuous and dispersed phases and upon the consequent difference in velocities of transmission of longitudinal acoustic waves. The technique was capable of providing information without time delay and continuously, which is especially useful in process control operations, but is limited to measuring small drop sizes (Bae and Tavlarides, 1989). Mitsis et al (1960) developed the scintillation technique which is based on the interface interaction between short range radio active particles and an immiscible phase. However, this technique had limited application because it required of high immiscibility between phases as well as suitable isotopes and target materials.

2.3.2 Direct Photographic Methods

Numerous methods have been used to measure interfacial area or drop size distribution, but they often fail to combine simplicity with accuracy. Photographic techniques are probably the most accurate, but the procedure requires many pictures and long times for analysis. Other techniques for determining interfacial area such as light transmittance, light scattering, scintillation and phase Doppler anemometry have been able to produced rapid results, but do not provide an absolute drop size distribution as photographic techniques. Skelland and Moeti (1990) deemed that this is a sufficient reason to determine drop sizes using photography instead of other indirect techniques. Photographs of drops can be taken directly through the vessel wall or by using optical probes to examine the interior of the vessel. An alternative photographic procedure is to remove samples of the dispersion for photography. There are numerous investigations that have employed photographic techniques for drop size measurement in liquid-liquid dispersions.
2.3.2.1 Photography Through Vessel Wall

Calabrese et al (1986a) and Wang and Calabrese (1986) employed a SLR camera with magnification capability. The camera was focused slightly above the impeller region and a high speed flash unit was fixed in the opposite end (outside the tank). Water-filled plexiglass box that surrounded tank served as a constant temperature water bath as well as means to eliminate optical distortion. However, the technique was successfully used in fairly low dispersed phase volume fractions, $\phi < 0.0015$ (Calabrese et al, 1986a) and $\phi < 0.002$ (Wang and Calabrese, 1986). Drop sizes produced during extraction experiments were determined from photographs of the dispersion taken through a plane glass water pocket (Skelland and Lee, 1981; Skelland and Moeti, 1990). Optical distortion was eliminated by a pocket filled with water (which was attached to the vessel wall). Diameters of drops produced by a homogenizer were measured by taking photographs through the tank wall with lighting provided by an electronic flash (Ohtake et al, 1987).

Kuriyama et al (1996) employed two photographic arrangements to measure drop sizes in a number of liquid-liquid dispersions. When taking photographs from the side wall of the vessel, images showed that drops overlapped, thus it was difficult to identify each drop individually. To eliminate this, images were taking between to glass probes interested from the top and bottom of the vessel. Comparison of results obtained from photographs taken from the side wall and the window within vessel showed some discrepancy. The frequency of drops which entered the window depended on the width of the window created by the glass probes. In all cases when photographs are taken at the vessel wall, the drops present in the images may not be representative of those in the bulk of the tank. The hydrodynamics of the wall region may be such as to give non-representative drop size distribution (Godfrey and Slater, 1994).

2.3.2.2 Photographic Probe

Brown and Pitt (1972) used an optical probe to obtain photographs of drops. A coating of the glass vessel rendered it to be optically inert. A flash used was through a window at the base of the vessel and the probe was located at the bottom of the vessel to obtain greater clarity of pictures. The arrangement was as such that the photographs were taken near the base of the
vessel. Brown and Pitt (1972) suggested that the size distribution of droplets at the vessel bottom was the same as that of other position in the vessel due to the non-coalescing nature of the system. Stamatoudis and Tavlarides (1985) employed a technique in which a light probe was placed at the bottom of the tank and a microscope probe capable of vertical movement was aligned at the top. The drops that appeared between the two probes were photographed using a camera attached to the microscope. Okufi et al (1990) used an endoscope attached to a camera and a light probe that was capable of producing drop images in virtually any location in the vessel. Similar technique was devised by Pacek and Nienow (1995). In their technique, a fibre optic lamp and an internally blackened light pipe was used for the measurement of drop size in concentrated dispersions. Many of the investigations mentioned above also examined the possibility of using a capillary technique for drop size measurement. However, the capillary technique failed to produce reasonable results in much of the experimental conditions (Okufi et al, 1990).

Ritter and Kraume (2000), Schulze et al (2000) and Kraume et al (2004) employed an endoscopic optical probe to measure drop sizes at high dispersed phase volume fractions. The light supply was integrated into the endoscope. The unit consisted of a flash light connected to an endoscope with fibre-optic light guides. A CCD-camera mounted at the upper end of the endoscope took pictures of the drops in the vicinity of the glass window. Similar endoscopic technique was used for the measurement drop sizes in a cadmium extraction process (Gallego-Lizon et al, 2000). In this case, the endoscope was attached to a high speed video camera and a high-powered light source, which allowed pictures to be taken at up to 1000 frames per second. Main advantage of video probe arrangement compared to taking image from outside vessel wall is its ability to measure drop size virtually at any location of vessel while dispersion is being stirred.

2.3.2.3 Sample Withdrawal and Photography

Perhaps the simplest way to measure the droplet size distribution in dispersion would be to place the sample on a microscope for photographing (Paul et al, 2004). Yang et al (2000) measured drop sizes in polymer dispersions by withdrawing samples to laboratory dish to be photographed using a microscope camera. To prevent coalescence of droplets aqueous solution of PVA was added. Ban et al (2002) used direct photographic method to measure
drop sizes in a mixer-settler extraction column. Liquid samples were drawn to a glass measuring cell where photographs were taken. Lagisetty et al (1986) investigated the breakage of non-Newtonian drops in dispersions. In their study drops were sized by simply withdrawing sample to optical microscope for measurement. Similar measurement technique was used to measure oil droplet in water (Al-Zuhair et al, 2004). A glass tube was used to withdraw samples for measuring drop sizes with an optical microscope (Kumar et al, 1991). At high dispersed volume fractions, there was considerable overlapping and crowding of drops, which made measurements difficult. To overcome this problem, samples were diluted and surfactant added before measurement. The photographic technique employed by Shimizu et al (1999) consisted of CCD camera attached to microscope. Samples were siphoned and poured into iced water or cold salad oil to freeze the drops rapidly.

Capillary tube (with a diameter several times larger than the largest drop) was used to withdraw sample from the vessel for photographing (Laso et al, 1987). Withdrawn samples were returned to the vessel once photographs were taken by a camera. Following which photographs were evaluated manually by a digitaliser. Godfrey et al (1977) employed a technique where samples were continuously withdrawn by means of a capillary tube with simultaneous photography of the dispersion as it leaves the tank.

### 2.3.2.4 Encapsulation and Photography

Drop diameter was also measured by the encapsulation method (Mlynek and Resnick, 1972; Tanaka, 1985). A device for trapping the droplet was immersed at the sampling position. It contained a chemical, thin polymer film or surfactant, which was able to encapsulate the droplets in the dispersion. Encapsulated drops then can be transferred to glass dishes for photography and measurement. This method cannot be used for some liquid-liquid systems due to the incompatibility of encapsulating materials and the liquids in the systems. Another disadvantage would be the influence of encapsulating chemicals on the drop size (Bae and Tavlarides, 1989). Tanaka (1985) found that the polymer film contributed up to 10% of the diameter of some droplets.
Table 2.2 lists several studies which have used the drop size measurement techniques discussed above. It also tabulates some experimental conditions used in the respective investigations.

Table 2.2: Drop sizes measurement techniques

<table>
<thead>
<tr>
<th>Authors</th>
<th>Measurement technique</th>
<th>T (tank diameter), cm</th>
<th>d_1 (Impeller diameter), cm</th>
<th>φ (volume fraction)</th>
<th>Continuous phase</th>
<th>Dispersed phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mitsis <em>et al</em> (1960)**</td>
<td>wcintillation</td>
<td>2.5-17.8</td>
<td>2.9 – 7.9</td>
<td>water</td>
<td>xylene</td>
<td></td>
</tr>
<tr>
<td>Sprow, F. B. (1967)</td>
<td>coulter counter</td>
<td>30</td>
<td>10</td>
<td>0.05-0.3</td>
<td>aqueous NaCl</td>
<td>iso-ocatane</td>
</tr>
<tr>
<td>Fernandes and Sharma (1967)</td>
<td>chemical method</td>
<td>10-86</td>
<td>0.33T-0.62T</td>
<td>aqueous caustic soda, aqueous NaOH</td>
<td>various formates, trichloroacetate</td>
<td></td>
</tr>
<tr>
<td>Brown and Pitt (1972)</td>
<td>photographic probe</td>
<td>30</td>
<td>10</td>
<td>0.05-0.3</td>
<td>water</td>
<td>kerosene</td>
</tr>
<tr>
<td>Mlynick and Resnick (1972)</td>
<td>encapsulation/photographic</td>
<td>29</td>
<td>10</td>
<td>0.025-0.34</td>
<td>water</td>
<td>carbon tetrachloride-isoctane</td>
</tr>
<tr>
<td>Godfrey and Grilic (1977)</td>
<td>photographic/capillary tube</td>
<td>15.2 (square tank)</td>
<td>5.10</td>
<td>0.05-0.5</td>
<td>water</td>
<td>kerosene, octanol, butanol</td>
</tr>
<tr>
<td>Narsimhan <em>et al</em> (1980)</td>
<td>coulter counter</td>
<td>14</td>
<td>7.6</td>
<td>0.001-0.005</td>
<td>water</td>
<td>CCl_4-ocatane, CCl_4-Anisol, chlorobenzene</td>
</tr>
<tr>
<td>Skelland and Lee (1981)*</td>
<td>photographic (through water pocket)</td>
<td>21,24.6</td>
<td>7.8, 10.6</td>
<td>&lt;0.09</td>
<td>water-sucrose</td>
<td>Dow corning fluid, ethyl acetate, benzaldehyde</td>
</tr>
<tr>
<td>Alwan <em>et al</em> (1983)</td>
<td>chemical method</td>
<td>8-10.3</td>
<td>4 - 4.9</td>
<td>0.15-0.075</td>
<td>water, aqueous NaOH</td>
<td>n-amyl acetate</td>
</tr>
<tr>
<td>Stamatoudis</td>
<td>photographic</td>
<td>24.5</td>
<td>10</td>
<td>0.025-</td>
<td>aqueous</td>
<td>kerosene, mineral</td>
</tr>
<tr>
<td>and Tavlarides (1985)</td>
<td>probes</td>
<td>0.15</td>
<td>glycerol oil</td>
<td></td>
<td></td>
<td></td>
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<td>----------------------</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eckert et al (1985)</td>
<td>light transmission</td>
<td>14-44</td>
<td>T/3-T/2</td>
<td>0.01-0.04</td>
<td>corn syrup-water</td>
<td>octanol, Oleic acid, nitrobenzene, xylene, kerosene, heptane, paraffin oil</td>
</tr>
<tr>
<td>Tanaka (1985)</td>
<td>encapsulation/photographic</td>
<td>12</td>
<td>5</td>
<td>0.1</td>
<td>water</td>
<td>sebacyl chloride-xylene-CCl₃</td>
</tr>
<tr>
<td>Legisetty et al (1986)</td>
<td>sample withdrawal photography</td>
<td>14.5</td>
<td>T/2</td>
<td>&lt;0.02</td>
<td>water, kerosene</td>
<td>polystyrene-styrene, CMC-water, aqueous CaCO₃</td>
</tr>
<tr>
<td>Calabrese et al (1986a)</td>
<td>photographic (direct)</td>
<td>14.2-39.1</td>
<td>T/2</td>
<td>φ&lt;0.0015</td>
<td>water</td>
<td>silicon oils</td>
</tr>
<tr>
<td>Wang and Calabrese (1986)</td>
<td>photographic (direct)</td>
<td>14.2-31.2</td>
<td>T/2</td>
<td>φ&lt;0.002</td>
<td>water-methanol</td>
<td>silicon oils</td>
</tr>
<tr>
<td>Skelland and Moeti (1990) **</td>
<td>photographic (through water pocket)</td>
<td>21.4</td>
<td>10</td>
<td>0.01</td>
<td>water</td>
<td>chlorobenzene, xylene, benzaldehyde</td>
</tr>
<tr>
<td>Okufi et al (1990)</td>
<td>photographic (direct)/endoscope</td>
<td>11-44</td>
<td>T/3</td>
<td>0.1-0.4</td>
<td>Water</td>
<td>heptane</td>
</tr>
<tr>
<td>Kumar et al (1991)</td>
<td>sample withdrawal photography</td>
<td>12.5</td>
<td>5.7</td>
<td>&lt;0.8</td>
<td>water</td>
<td>toluene</td>
</tr>
<tr>
<td>Pacek and Nienow (1995)</td>
<td>photographic and capillary/light transmittance</td>
<td>15</td>
<td></td>
<td>&lt;0.45</td>
<td>chlorobenzene</td>
<td>water</td>
</tr>
<tr>
<td>Study</td>
<td>Technique/Description</td>
<td>Frequency</td>
<td>Time Interval</td>
<td>Inertial Diameter</td>
<td>Solvent System</td>
<td>Additional Details</td>
</tr>
<tr>
<td>------------------</td>
<td>-------------------------------------------------</td>
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<td>-------------------</td>
<td>-------------------------------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>Kuriyama et al (1996)</td>
<td>Photographic probe</td>
<td>12.7, 18.6</td>
<td>T/2</td>
<td>0.002-0.03</td>
<td>water-PVA or NaCl</td>
<td>silicon oil and tetrabromomethane</td>
</tr>
<tr>
<td>Zhou and Kresta (1998)</td>
<td>Phase doppler anemometry</td>
<td>24</td>
<td>T/4-T/2</td>
<td>&lt;0.0003</td>
<td>water</td>
<td>silicon oil</td>
</tr>
<tr>
<td>Shimizu et al (1999)</td>
<td>Sample withdrawal photography</td>
<td>9</td>
<td>4.9</td>
<td>&lt;0.005</td>
<td>aqueous CMC or xanthan gum</td>
<td>palm oil</td>
</tr>
<tr>
<td>Schultze et al (2000)</td>
<td>Endoscope (light integrated)</td>
<td>19-40</td>
<td>0.3T – 0.5 T</td>
<td>0.05-0.5</td>
<td>water</td>
<td>toluene</td>
</tr>
<tr>
<td>Gallego-Lizon et al (2000)</td>
<td>Endoscope (light integrated)</td>
<td>9</td>
<td>3.6-8.5</td>
<td>0.025-0.067</td>
<td>cadmium-phosphoric acid</td>
<td>cynex-kerosene</td>
</tr>
<tr>
<td>Yang et al (2000)</td>
<td>Sample withdrawal photography</td>
<td>14.4</td>
<td>T/2</td>
<td>0.05-0.1</td>
<td>water-PVA</td>
<td>styrene</td>
</tr>
<tr>
<td>Willie et al (2001)</td>
<td>Phase doppler anemometry</td>
<td>13.4</td>
<td>T/3</td>
<td>0.002</td>
<td>water</td>
<td>silicon oil</td>
</tr>
<tr>
<td>Kraume et al (2004)</td>
<td>Endoscope (light integrated)</td>
<td>15, 30</td>
<td>0.3T – 0.5T</td>
<td>0.05-0.5</td>
<td>water</td>
<td>anisole, butyl acetate, tetralin, toluene</td>
</tr>
<tr>
<td>Al-Zuhair et al (2004)</td>
<td>Sample withdrawal photography</td>
<td>9</td>
<td>5</td>
<td>0.05-0.5</td>
<td>water</td>
<td>palm oil</td>
</tr>
</tbody>
</table>

* Extraction process – solute used heptanoic acid
** Extraction process – solutes used heptanoic, nonanoic, and benzoid acid
* Extraction process – solute – nitric acid
** Impeller was arranged vertically for some experiments
2.4 Impeller Types for Agitation

Power number, flow number, shear levels, and flow patterns characterise various impellers available for dispersive operations. One approach to classifying these devices would be in terms of the relative amounts of flow and shear delivered by each device. An impeller can be designed and operated such that its power input is used to maximise flow with minimal shear, maximise shear with minimal flow or provide a balance between the two (Myers et al, 1999). Figure 2.13 shows flow and shear relationship for various types of impellers.

![Impeller Types Diagram](image)

Figure 2.13: For a given power input, the flow and shear relationship of various impellers (Oldshue, 1983).

The figure provides a rough guide to the selection of impeller type for a particular application. At the top of the list are impellers with high flow and low shear rates. These are paddle types and large diameter gates and helical models. Such impellers are best suited for high-viscosity blending (Oldshue, 1983). Next are axial flow impellers. These include marine propeller and pitched turbines, which are generally used for solid suspension, blending and heat transfer. Radial flow impellers are listed next and are used most often for gas-liquid and liquid-liquid mass transfer operations. For application requiring extremely
high shear rates, narrow-bade impellers are used. These include saw-tooth impellers and bar turbines.

The discharge characteristics of an impeller determine the recirculation patterns of the fluid. As a result, very different flow patterns are generated by different impellers. This has been often used as a mean to classify various impellers. Radial devices discharge a fluid in a horizontal (radial) direction to the vessel wall; whereas axial-flow impellers create a flow parallel to the impeller shaft (Oldshue, 1983). Some typical flow patterns of a radial and an axial flow devices operating with a Newtonian liquid in the turbulent region are illustrated in Figure 2.14.

![Figure 2.14: Flow patterns for radial (a) and axial (b) flow impellers with baffles (Harnby et al., 1992).](image)

The propeller (Figure 2.14b) creates a mainly axial flow through the impeller and the central axial flow may be upwards or downwards depending upon the direction of the rotation. In contrast the flat-bladed turbine (Figure 2.14a) produces a strong radial flow outwards form the impeller, creating a circulation zones in the top and bottom of the tank (Harnby et al, 1992). Radial flow impellers such as the Rushton turbine, while providing flow also generate significant shear. These impellers are employed in dispersing immiscible fluid phases (gas/liquid and liquid/liquid) typically for interphase mass transfer (Myers et al, 1999). Examples of radial flow impellers include the disk style, flat blade and curved blade.
impellers. Axial flow impellers can discharge material radially as well as axially. The major applications for axial flow impellers have been in blending and solid suspension applications where the axial flow of the impeller sweeps the solids off the tank bottom (Tatterson, 1991). The pitched blade turbine and the propeller are common axial flow impellers.

Flow patterns in an agitated vessel not only depend on the type of impeller but also on the characteristics of the fluid, size and proportion of the tank and baffle geometry. Viscosity produces one of the more subtle effects on flow patterns (Dickey and Hemrajani, 1992). With increasing viscosity, the discharge from the impeller is less effective in inducing circulation motion. As the strength of return flow to the impeller diminishes, axial flow is more difficult to achieve. The result of increased viscosity is an eventual radial flow pattern with almost any style of impeller. Variation in the ratio of the diameter of the impeller to that of tank ($d_l/T$) results in changes to flow patterns. Small $d_l/T$ generates intense agitation in the impeller region and a large, less intense recirculation patterns. An increase in $d_l/T$ results in a more intense recirculation flow in the tank.

Tatterson et al (1991) classifies impellers according to mixing regime: laminar or turbulent mixing. Axial and radial flow impellers are typically used in low-viscosity fluids hence classified as turbulent impellers. These are generally not recommended for application dealing with highly viscous liquids (Paul et al, 2004). Their use will results in the formation of caverns around the impeller. Mixing can be good inside cavern, but poor outside. Also flow patterns flatten out and axial flow impellers produce radial flow. These flow changes diminish blending quality significantly. Thus for application dealing with high viscosity fluids, close clearance or laminar impellers are recommended. Typical laminar flow impellers are helical ribbons, screws, and anchor impellers (Tatterson, 1991). These impellers act directly on large proportion of the material and do not rely on induced motion to bring about mixing action (Dickey and Hemrajani, 1992).
2.4.1 Power and Flow Number

All the power supplied to a mixing system produces internal circulation, \( Q \), and velocity head, \( H_v \), which provides shear in mixing (Paul et al., 2004). The circulation capacity of a mixing system is represented by a dimensionless expression called flow number or flow coefficient or pumping number, \( N_Q \):

\[
N_Q = \frac{Q}{N d_I^3}
\]  

(2.71)

The flow number depends on the impeller type, \( d_I / T \) ratio and impeller Reynolds number (\( N_{Re} = \rho N d_I^2 / \mu \)). Figure 2.15 shows the flow number of pitched bladed turbine at various \( N_{Re} \).

![Figure 2.15: Flow number versus \( N_{Re} \) for pitched blade turbines (Paul et al., 2004)](image)

It is evident from the above Figure that smaller \( d_I / T \) produces higher flow number. In addition \( N_Q \) increases as \( N_{Re} \) increases up to \( N_{Re} \) of \( 10^4 \) and becomes constant in turbulent conditions. Flow number of an impeller also changes with changes in impeller geometry. Values of flow numbers for commonly used impellers under turbulent conditions are listed in Table 2.3.
Table 2.3: Flow number, $N_Q$ for various impellers (Paul et al., 2004).

<table>
<thead>
<tr>
<th>Impeller type</th>
<th>$N_Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propeller</td>
<td>0.4-0.6</td>
</tr>
<tr>
<td>Pitched blade turbine</td>
<td>0.79</td>
</tr>
<tr>
<td>Hydrofoil impellers</td>
<td>0.55-0.73</td>
</tr>
<tr>
<td>Retreat curve blade</td>
<td>0.3</td>
</tr>
<tr>
<td>Flat-blade turbine</td>
<td>0.7</td>
</tr>
<tr>
<td>Rushton turbine</td>
<td>0.72</td>
</tr>
<tr>
<td>Hollow blade turbine</td>
<td>0.76</td>
</tr>
</tbody>
</table>

The power consumed by a mixer can be expressed by the following:

$$ P = \frac{N_p \rho N^3 d_i^5}{g} $$

Parameter $N_p$ is known as the power number and is analogous to a friction factor or drag coefficient (McCabe et al., 1993). The number depends on impeller type and tank geometry as well as impeller Reynolds number. Figures 2.16 and 2.17 shows the relationship between $N_p$ and $N_{Re}$ for several different impellers.

Figure 2.16: $N_p$ vs $N_{Re}$ for various impellers (Paul et al., 2004).
It is evident from the above correlations that under turbulent conditions ($N_{Re} > 10^4$) the power number remains constant for a given impeller geometry. In laminar conditions ($N_{Re} < 10$) the power number appears to increase with decreasing Reynolds number. The slope of the curve in the laminar region depends on the system geometry (Harnby et al, 1992). In the transitional region between laminar and turbulent conditions, no simple mathematical relationship exists between $N_P$ and $N_{Re}$.
2.5 Reactor Design

2.5.1 Agitated Liquid-liquid Reactors

A variety of industrially important reactions such as nitration, sulfonation, alkylation, reduction etc., involves two liquid phases (Vasudevan and Sharma, 1984). Despite their importance, design of liquid-liquid reactors has received very limited attention as compared to other heterogeneous systems such as gas-liquid and solid-liquid systems (Perry and Green, 1998). Liquid-liquid reactions can be carried in several modes of operations: batch, semi-batch or continuous. Mechanically agitated contactors are used for batch and semi-batch operations, whilst spray columns, packed columns, plate columns, multistage mechanically agitated contactors, centrifugal extractors, etc., are usually used for continuous operations (Vasudevan and Sharma, 1984). The important design parameter is the time of reaction for a specified degree of conversion for batch operations and volume/height of the reactor for the continuous mode of operation.

Liquid-liquid reactors required intimate contact between the two liquid phases to ensure adequate rates of interphase mass transfer and/or chemical reaction. This is usually conducted by dispersing one phase as drops in the second, continuous phase (Bae and Tavlarides, 1989). Mechanically agitated tanks are favoured for these kinds of operations because the interfacial area can be made large (Perry and Green, 1998). In the case of the present investigation, PIBSA derivative emulsifier is typically produced in mechanically agitated stirred tank operating in a batch mode. Therefore subsequent discussions will focus on batch reactors.

2.5.2 Batch Reactors

The batch reactor is widely used in chemical industry because of its flexibility. It is often characterised as a flexible and multipurpose equipment. That means that the same apparatus is used to carry out different reactions and operations under various operating conditions (Le Lann, et al, 1999). Because of its greater flexibility, batch reactors are well suited to the manufacture of products subjected to fluctuations in market conditions. So the use of batch reactors for the production of low volume, high value products such as pharmaceuticals,
polymers, biotechnological or other fine chemicals has never been supplanted by continuous processes (Garcia et al, 1995).

2.5.2.1 Design Equation

The starting point for the development of the basic design equation for a batch reactor would be to perform a material balance involving one of the reactants. A batch reactor has no input or output of mass after initial charging. The amount of individual components may change due to the reaction, but not due to flow into or out of the system. Thus the reactor design equation for an ideal batch reactor can be expressed as (Hill, 1977):

$$\frac{dN_A}{dt} = (-r_A) V \quad (2.73)$$

The term on the left is the rate of accumulation of reactant A within the reactor (of volume, V) and term in the right is the rate of disappearance of reactant A within the reactor by chemical reaction. Former term may be written terms fraction of conversion ($f_A$) and thus equation (2.73) becomes:

$$N_{A0} \frac{df_A}{dt} = (-r_A) V \quad (2.74)$$

Where $N_{A0}$ is the number of moles of species A present when the fraction of conversion is zero. Rearrangement and integration of equation (2.74) gives batch time:

$$t_1 - t_2 = N_{A0} \int_{f_{A1}}^{f_{A2}} \frac{df_A}{(-r_A) V} \quad (2.75)$$

Where $f_{A1}$ and $f_{A2}$ represent the fraction conversion at times $t_2$ and $t_1$ respectively. This equation is the most general form the basic design relationship for a batch reactor (Hill, 1977). The design equation (2.75) is valid for both isothermal and nonisothermal operation as well as for constant volume and constant pressure operations. For the design equation to
Chapter 2

be valid for the entire content of the reactor (ideal reactor), following characteristics are assumed (Nauman, 2002):

- Reactants are quickly charged, mixed and brought to temperature at the beginning of the reaction cycle.
- Mixing and heat transfer are sufficient to assure that the batch remains completely uniform throughout the reaction cycle.

An ideal batch reactor has no temperature or concentration gradient within the system volume. Concentration will change with time because of the reaction, but at any time it is uniform. Similarly, in the case of a nonisothermal reactor, temperature will change with time, but is uniform at any particularly time. The reactor design expressions for homogeneous systems is well established and has a simple form, but this not the case for heterogenous systems.

2.5.2.2 Design Equations Heterogeneous Reactors

Design of an industrial reactor with two fluid phases may be relatively complex if all variables are to be taken into account. In heterogenous systems, necessary consideration must be given to mass transfer and chemical kinetics and the mechanism of the chemical reaction. These steps are influenced by the reactor configuration and operating conditions. Therefore an understanding of these interactions is crucial to the optimisation of the process (Kolaczkowski et al, 1999). Furthermore, better understanding of the performance would be attained if the mechanisms behind the process occurring in the reactor could be elucidated and the complex nature of their interdependence is identified. In section 2.1.2 of this chapter, some concepts of reaction regimes were outlined. For liquid-liquid reactions, location of the kinetic regime depends on the relative rates of rate of reaction and mass transfer, typically residing in the film for fast reactions and in the bulk of the liquid for slow reactions (Levenspiel, 1972). Overall rate equations often require knowledge of mass transfer coefficients, interfacial area, diffusivities, solubilities and reaction kinetics of the system. However, one is often limited by the lack of data for these variables (Trambouze et al, 1988). To the author’s best knowledge, detailed kinetic study of MEA-PIBSA reaction is not available in the open literature. This is the case for many heterogeneous systems including
wet air oxidation for wastewater treatment (Kolaczkowski et al, 1999). As such, reactor design is typically based on empirical methods and global rate expressions. However such techniques are only adequate over a range of operating conditions investigated.

Design equations for liquid-liquid reactors are sparse at best, but some have attempted to produce mathematical models for these cases. Vasudevan and Sharma (1984) provided several design equations for liquid-liquid reactors operating in batch mode. The mode relevant for the present system would be their case (iii) in which the dispersed phase was pure and the product was insoluble in the dispersed phase. The batch time for complete disappearance of droplets can be calculated from the following equations.

For a case where slow or fast pseudo first-order reaction with respect to B:

\[
\frac{1}{a_i V_{di}^{2/3} V_m A} \left( \frac{D_A k_2 Z[A_o]}{V_C} \right)^{1/2} \int_0^{v_{di}} \frac{dV_d}{V_d^{2/3} \left( \frac{V_C [B_o]}{Z[A_o]} - V_{di} + \frac{k_2^2 V_C}{D_A k_2 Z[A_o]} \right) + V_d}^{1/2}
\]

For instantaneous reactions:

\[
\frac{1}{a_i V_{di}^{2/3} V_C} \left( \frac{D_B}{D_A} \right)^{1/2} \int_0^{v_{di}} \frac{dV_d}{V_d^{2/3} \left( \frac{V_C [B_o]}{Z[A_o]} - V_{di} + m_A V_C \frac{D_A}{D_B} \right) + V_d}^{1/2}
\]

\[
(2.76)
\]

\[
(2.77)
\]

where \( t_b \) = Total batch time, s
\( a_i \) = Initial interfacial area, m\(^2\)/m\(^3\)
\( V_{di} \) = Initial volume of dispersed phase, m\(^3\)
\( D_A \) = Diffusivity of A in B phase, m\(^2\)/s
\( m_A \) = Distribution coefficient of A between phases
\( k_2 \) = Second order rate constant, m\(^3\)/mol.s
\[ V_d = \text{Volume of dispersed phase, m}^3 \]
\[ V_C = \text{Volume of continuous phase, m}^3 \]
\[ A_o = \text{Concentration of A in dispersed phase, mol/m}^3 \]
\[ [B_0]_i = \text{Initial concentration of B in continuous phase, mol/m}^3 \]
\[ k_c = \text{Continuous phase mass transfer coefficient, m/s} \]
\[ Z = \text{Stoichiometric factor} \]
\[ D_B = \text{Diffusivity of B in A phase, m}^2/\text{s} \]

In the development of these equations several assumptions were made:

- Liquid phases are completely backmixed
- The physical properties of liquids remain unchanged
- System is isothermal

Assumption of isothermal operating conditions can be justified because of the ease of heat removal in liquid-liquid reactors (Vasudevan and Sharma, 1984). However, the other two assumptions cannot be easily justified. As the reaction proceeds with time, product of varying physical properties (density, viscosity...etc) could be formed. As such one would expect the physical properties of the phases to change with time. Despite the lack of applicability of the equations to real batch reactor design, the equation does illustrate the complexity of liquid-liquid reactor design. Mass transfer coefficients, solubilities, diffusivities, reaction rate constant and interfacial areas are required for the reactor design.

Based on the analogies of gas-liquid reactor design Rose (1981) developed an equation which can be used to model liquid-liquid reactions.

\[
\frac{dN_B}{dt} = E' k_c a \left( \frac{C_A}{C_{A_0}} \right)^{2/3} V \left[ \left( C_B \right)_{\text{phase}_2} - \left( C_B \right)_{\text{phase}_1} H_A \right] - k V (1 - \phi) C_A \left( C_B \right)_{\text{phase}_1}
\]

(2.78)

where
\[ V = \text{volume of reactor, m}^3 \]
\[ H_A = \text{distribution coefficient between phases} \]
\[ E' = \text{enhancement factor} \]
\[ k = \text{reaction rate constant (for second order, m}^3/\text{mol.s)} \]
\[ \phi = \text{dispersed phase volume fraction} \]
\[ k_L = \text{mass transfer coefficient, m/s} \]
\[ (C_B)_i = \text{concentration of reactant B in phase i, mol/m}^3 \]
\[ C_A = \text{concentration of reactant A, mol/m}^3 \]
\[ C_{Ao} = \text{initial concentration of A, mol/m}^3 \]
\[ a = \text{interfacial area, m}^2/m^3 \]

For an extreme case, where the system is mass transfer controlled or reaction kinetics controlled this model takes the following form.

For kinetically controlled systems:

\[
\frac{dN_A}{dt} = -V(1 - \phi)k_l H_B (C_B)_{phase1} \tag{2.76}
\]

For mass transfer controlled systems:

\[
\frac{dN_A}{dt} = -E'k_L a \left( \frac{C_A}{C_{Ao}} \right)^{2/3} V(C_B)_{phase2} \tag{2.77}
\]

If the dispersed phase is a pure component B, then the quantity available to be dispersed is reduced proportionally as the conversion of the reaction increases. If this reduces the drop size rather than the number of drops, then the surface area during the reaction can be related to the initial area by \( a(C_A/C_{Ao})^{2/3} \) when the reactor is fed with a stoichiometric quantity of B (Nagata, 1975). This relationship was found to be inapplicable for ester-alkali reaction by Hiraoka et al (1990) who were one of few investigators to conduct a drop size study in reactive liquid-liquid dispersions. They found that the Sauter mean diameter, \( d_{32} \) is was constant during the reaction period although the number of droplets decreased with time.

Although there is some information of liquid-liquid reactor design available in the literature, this area is highly underdeveloped. Furthermore, a literature survey on liquid-liquid reactor design revealed that a reasonable model for producing a quantitative solution to the liquid-
liquid reactor (agitated batch reactor) design problem is lacking. However, Trambouze et al (1988) suggests that it is possible to state that a body of semi-quantitative data could provide a reasonable guidance for the design of liquid-liquid reactors.

Various aspects of liquid-liquid reactions are discussed in the above sections. Much of the discussion have focused on the various parameters that constitutes the overall rate equation, including mass transfer coefficients, reaction kinetics and interfacial area. It is evident from the current body of knowledge that experimental information of these parameters are lacking with the exception of a limited number liquid-liquid systems. This is despite the fact liquid-liquid reactions are numerous and have an important role in chemical industry. Present investigation examines one such liquid-liquid system which is used in the emulsion explosives industry. This study will focus on one of the most important components in the overall rate equation, interfacial area.
This chapter details the equipment and material used to conduct experiments. Liquid properties, reactor setup and experimental procedures for the determination of drop sizes and reactant concentrations are discussed.
3.0 Introduction

The present study is an investigation on the production of an emulsifier. It is produced by the reaction of two immiscible liquids, namely PIBSA (Polyisobutylene succinic anhydride) and MEA (monoethanolamine). The reaction is carried out by mechanical agitation in a stirred tank reactor. As discussed in the earlier chapters, the project aims to examine some aspects of the design of a liquid-liquid reactor. This requires the measurement of several parameters that embodies the liquid-liquid reactive system. These are as follows:

- Drop size
- Reaction
- Viscosity
- Interfacial tension
- Density

This chapter presents the details of the experimental equipment and procedure required to obtain such information. As mentioned previously, the measurements for this system were quite difficult to obtain due to the complexities of the system. In addition, liquid-liquid reactive systems such as the present have rarely been studied. As such, some aspects of the experimental work were unprecedented and to authors best knowledge the emulsifier production system has not been subjected to such a study in the past. The initial sections of this chapter will detail the materials involved in the system and the design of the laboratory reactor. Specific experimental techniques and procedures will be discussed in the subsequent sections.
3.1 Materials

Materials used in the emulsifier production were the reacting components, PIBSA and MEA and the non reactive component, mineral oil. The latter was used to dilute the PIBSA to form the continuous phase.

3.1.1 Polyisobutylene Succinic Anhydride (PIBSA)

PIBSA is more commonly known for its use as a raw material in the synthesis of ashless dispersant, which is an important class of lubricating oil additive (Harrison et al, 2002). The PIBSA molecule contains a branched polyisobutylene (PIB) chain attached to anhydride ring (Figure 3.1).

![Figure 3.1: Molecular structure of PIBSA](image)

PIBSA produced by Chevron Orinite Australia, was supplied for the present investigation by Orica Specialty Chemicals. It has a molecular weight range of 400 -5000 and an average molecular weight, $M_w$ of 1085 g/mol. The PIB chain comprises of an average backbone carbon number of approximately 30. Some of the physical properties of PIBSA are given in Table 3.1.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, $\rho$, @ 23 °C</td>
<td>925 kg/m$^3$</td>
</tr>
<tr>
<td>Viscosity, $\mu$, @ 20 °C</td>
<td>46.5 Pa.s</td>
</tr>
<tr>
<td>Surface tension, $\gamma$, @ 23 °C</td>
<td>41.2 mN/m</td>
</tr>
<tr>
<td>Boiling point*</td>
<td>&gt;316 °C</td>
</tr>
<tr>
<td>Flash point *</td>
<td>185 °C</td>
</tr>
</tbody>
</table>

* Obtained from Orica Specialty Chemicals material and safety data sheet.

Density, viscosity and surface tension measurement details are given in sections 3.5 to 3.7.
As discussed in Chapter 1, PIBSA is a product of the *thermal ene reaction* (chemical reaction between an alkene with an allylic hydrogen and a multiple bond) between maleic anhydride and polyisobutylene. PIBSA has a dark amber appearance with a mild odour and is extremely viscous at room temperature. General inspection of the substance would indicate a consistency and appearance of thick honey. During the course of the investigation, rheological tests were conducted and viscosities of PIBSA at various temperatures were obtained (Figure 3.2). To the author’s best knowledge no such data was available in the open literature. Most polymer solutions exhibit non-Newtonian behaviour (Kissa, 1999). However, viscosity test has shown PIBSA to exhibit Newtonian Characteristics (see Appendix A.1 for shear rate vs shear stress plot).

![Figure 3.2: Viscosity of PIBSA at various temperatures.](image)

PIBSA is capable of reacting with various polyamines and this was the subject of several investigations (Chottopadhyay *et al* 1992; Gaicha *et al*, 1993; Ghaicha *et al*, 1995; Tomlinson *et al*, 1997; Al-Sabagh and Atta, 1999; Reynolds *et al*, 2004). It is also able to react with atmospheric water vapour to form a diacid, shown in the reaction scheme in Figure 3.3. Typically there is a certain quantity of diacid present in every batch of PIBSA, which can be detected in FTIR analysis. The diacid undergo further reaction with polyamines, in this case MEA, to form a product as shown in the reaction scheme. Formation of such
impurity in the emulsifier product should be minimised. Therefore actions were taken to ensure that PIBSA was stored in conditions where the likelihood of acid formation was minimal.

![Reaction scheme of diacid formation and further reaction with MEA.](image)

**Figure 3.3: Reaction scheme of diacid formation and further reaction with MEA.**

### 3.1.2 Mineral Oil

Refined mineral oil was mixed with PIBSA to form the continuous phase. The mineral oil (Shell P833) was produced by Shell Australia, and provided by Orica Specialty Chemicals for the study. Shell P833 consists of 5%, 63% and 32% of aromatic, paraffin and naphthenic hydrocarbons respectively. The complex mixture of hydrocarbons had a substantially lower viscosity than PIBSA (see Appendix A.1 for PH833 viscosity vs temperature). Thus it was able reduce the viscosity of the continuous phase to a manageable level (see Appendix A.1 for continuous phase viscosity vs temperature). PIBSA was able to readily mix with the mineral oil to form the homogeneous phase. Properties of the mineral oils were as such that it was equally capable of forming a homogenous mixture with the emulsifier produced in the reaction.
Table 3.2: Properties of Shell P833

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, $\rho$, @ 23 °C</td>
<td>857 kg/m$^3$</td>
</tr>
<tr>
<td>Viscosity, $\mu$, @ 20 °C</td>
<td>0.049 Pa.s</td>
</tr>
<tr>
<td>Surface tension, $\gamma$, @ 23 °C</td>
<td>40.1 mN/m</td>
</tr>
<tr>
<td>Boiling point*</td>
<td>&gt;360 °C</td>
</tr>
<tr>
<td>Flash point *</td>
<td>210 °C</td>
</tr>
</tbody>
</table>

* Obtained from Orica Specialty Chemicals material and safety data sheet.

Density, viscosity and surface tension measurement details are given in sections 3.5 to 3.7.

3.1.3 Monoethanolamine (MEA)

Monoethanolamine, MEA or 2-aminoethanol is a bifunctional molecule because it contains both alcohol and amine functional groups in the same compound. The molecular structure of the compound is shown in Figure 3.4.

\[
\text{HOCH}_2\text{CH}_2\text{NH}_2
\]

Figure 3.4: Molecular structure of MEA

MEA is often recognised as the solvent used in natural gas purification process, but as discussed in the introduction it has numerous other commercial uses. Therefore, unlike PIBSA, MEA has been the subject of numerous research works. AJAX Finechem high grade MEA was used for the present investigation. Some of the physical properties of monoethanolamine are given in Table 3.3.

Table 3.3: Properties of MEA

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, $\rho$, @ 23 °C</td>
<td>1014 kg/m$^3$</td>
</tr>
<tr>
<td>Viscosity, $\mu$, @ 20 °C</td>
<td>0.024 Pa.s</td>
</tr>
<tr>
<td>Surface tension, $\gamma$, @ 23 °C</td>
<td>63.6 mN/m</td>
</tr>
<tr>
<td>Mol. Wt*</td>
<td>61.08 g/mol</td>
</tr>
<tr>
<td>Boiling point*</td>
<td>171 °C</td>
</tr>
<tr>
<td>Melting point *</td>
<td>10.5 °C</td>
</tr>
</tbody>
</table>

*Obtained from Perry and Green (1998)

Density, viscosity and surface tension measurement details are given in sections 3.5 to 3.7.
3.2 Experimental Reactor Setup

In designing the laboratory scale reactor, several factors to be taken into account. The reactor should in some ways reflect the configuration of the plant reactor. In order to draw meaningful conclusions and comparisons between this study and others, vessel geometries should also be similar those typically used in previous investigations. Availability of raw materials and experimental design was also a major consideration. Heterogenous liquid-liquid reactor design is an extremely complex process and as discussed in the introduction there are a number of parameters that need to be examined during the present investigations. This involves several measurements during the reaction process including drop size, reactant and product concentrations, viscosities, densities and interfacial tensions. The reactor setup should be able to accommodate these measurements. After giving careful consideration to all these factors, a reactor was designed and constructed as shown schematically (Figure 3.5).
Figure 3.5: Schematic of the laboratory scale reactor used in experiments.
The size of the stirred tank, 15 cm in diameter, could be considered to be typical for liquid-liquid studies. Most of the studies on drop size have been conducted in vessels about 10 to 15 cm in diameter (Table 2.2). The vessel used in the present investigation was constructed with glass due to its corrosion resistance and easiness to clean. Other design aspects of the tanks such as the impeller clearance \( C_L = T/3 \) and impeller diameter \( d_I = T/3 \) were also of the standard geometry used in most drop size studies. However, it should be noted that some researchers used impeller diameter, \( d_I = T/2 \) (Yang et al., 2000; Lagisetty et al., 1986; Calabrese et al., 1986a, Kuriyama et al., 1996) and impeller clearance, \( C_L = T/2 \) (Tanaka, 1985; Calabrese et al., 1986a; Kuriyama et al., 1996; Shimizu et al., 1999) for their studies. The baffle width is usually from \( T/10 \) to \( T/12 \) and should be located at a minimum distance of \( T/72 \) from the vessel wall (Paul et al., 2004). Displacing the baffles by a small distance from the bottom and sides of tank enables the liquid to pass between the baffle and the wall. The dimensions of the baffles in the present investigation were well within those recommended in the literature. The 4 equally spaced baffles were constructed from copper-alloy due to the fact they can easily be cleaned.

Two impellers were used in the present investigation; 6-bladed Rushton turbine and 3-bladed marine propeller. Dimensions of these impellers are shown in Figure 3.6. Rushton turbine has been employed in most liquid-liquid mixing studies as a standard impeller, hence was chosen for the present investigation. For comparing the effect of impellers it was important to employ an impeller different to the Rushton, which is a radial-flow impeller. Thus marine propeller which is an axial-flow impeller was chosen this study. Both impellers and the impeller shaft were constructed from stainless steel because the material is corrosion resistant and easy to clean. Agitation was provided by IKA Eurostar Power Control-Visc laboratory overhead motor. It was capable of operating at speeds in the range of 50-2000 rpm. A LCD screen on the unit allowed the operating speed to be monitored. Tachometer measurements taken during the experiments showed that the displayed speed was within \( \pm 3 \) rpm.
3.2.1 Standard Experimental Procedure

The first step in the experimental procedure was the preparation of the continuous phase and this was done by mixing the measured volumes of PIBS/oil. The volume fractions of PIBS and mineral oil were 0.545 and 0.427 respectively. As in the case of standard mixing vessels, the liquid height was equal to the tank diameter. The liquids were mixed at a stirrer speed of 600 rpm until the mixture was relatively homogeneous. Then the reactor was immersed in a water bath. The bath consisted of an Eski with water level slightly above liquid height in the vessel. Cooling or heating was provided by a chiller unit (Julabo F30). In this arrangement, water from the bath can be pumped to the chiller unit where sensor detects the inlet temperature. Depending on the desired temperature of the bath, the water was cooled or heated by the chiller before being pumped back to the water bath. Temperature of the water bath and the reactor was monitored using standard mercury
thermometers. At room temperatures of 20 ±10°C, the temperature control system was effective in maintaining the desired reactor temperature of 20 ± 2°C. The only exception was at 600 rpm when the reactor temperature increased up to 25°C in the initial stages of the experimental run.

After the initial period of agitation visual inspection showed that a significant number air bubbles were trapped within the contents of the vessel. Given the viscosity of the fluids, air entrapment during the filling process was unavoidable. To allow entrapped air bubbles to escape, the mixture was allowed to remain still for period of time 1-2 hours. When all of the air bubbles have escaped, the mixture was agitated again at 500 rpm until it attains complete homogeneity. At this point the chiller unit was turned on and the temperature was set to 20 ºC. As soon as the temperature of the reactor reached the desired value, the stirrer speed was set to the required level. Then the required volume of MEA was poured rapidly into the vessel in the vicinity of the impeller shaft to commence the reaction.

All measurements were carried out using the samples withdrawn in the impeller region as shown in Figure 3.5. There have been differing views of weather the impeller region is representative of conditions throughout the tank. Tanaka (1985) found that the local drop diameter varies with location, whereas Brown and Pitt (1972) proposed that drop size distribution in the impeller region is the same as that of any other position in non-coalescing systems. Many other studies have assumed that in dilute dispersions (systems with low dispersed phase volume fraction) coalescence is negligible and therefore sampling in the impeller region was used.

Depending on the experimental conditions and measurement technique, certain number of samples were taken during the experimental run. All runs were completed within a period of 3 hours. At the end of the experiment, the contents of the reactor were disposed and the vessel was cleaned. To clean the vessel, it was firstly rinsed with hexane to dissolve the chemical layer that remains on the vessel wall. Once dissolved, the solution was disposed and the vessel was soaked in hot water and then in household detergent for a certain period of time. This was followed by repeated rinsing using hot water until all impurities were removed. Then the vessel was rinsed with methanol and then with distilled water. Finally, it was dried in a vacuum oven at 120°C for approximately an hour. Impeller shaft, removable baffles, impeller and other laboratory ware were also cleaned using a similar procedure. The
standard experimental procedure was followed for all experimental runs. Sampling technique varied slightly with the measurements that were taken. These will be discussed in detail in subsequent sections of this chapter.

### 3.3 Drop Size Measurement

The experimental measurement of drop sizes is well-established and numerous techniques have been developed. Section 2.3 gives the details of various measurement techniques that have been used in previous drop size studies. In most cases, except for some measurements at low dispersed phase volume fractions, it is correct to use the term *estimate* of drop sizes given that most of the techniques have one or more limitations (Godfrey *et al*, 1994).

To the author’s best knowledge, the liquid-liquid system involved in the present study, i.e., MEA-PIBSA/mineral oil system, has not previously been subjected to a drop size investigation. Compared to the other systems listed in Table 2.2, the present system is unusual in some aspects. The system has a continuous phase viscosity that is much higher than those liquid used in other studies. Most of the investigations dealt with fluids with viscosities in the range of 10-0.01 cP. However, experiments conducted by Shimizu *et al* (1999) and Stamatoudis and Tavlarides (1985) dealt with liquids with continuous phase viscosities of up to 2.1 Pa.s and 0.33 Pa.s respectively. The continuous phase viscosity in the present investigation is expected to range from approximately 1 Pa.s to 12 Pa.s.

The main requirements for the drop size measurement technique for the present study are:

a) It should be able to measure drop sizes with a dispersed volume fraction of at least 0.028, which is the amount of MEA required for an equimolar reaction. In addition, drop sizes are required at several other dispersed phase volume fractions, possibly as low as 0.005.

b) It should be able to measure drop size distributions at several stages during the course of the reaction.

c) It should be able to measure drop size for several impeller speeds and types.

d) The interference to the hydrodynamics of the system and the reaction due the instrumentation of the technique should be minimal.
As discussed in chapter 2 there are numerous drop size measurement techniques that have been developed over the years. They have generally been developed for specific liquid-liquid systems and often cannot be applied to other systems. Given the fluid properties for the present system and the requirement listed above, some of the drop size measurement techniques discussed in the literature cannot be employed for the present system. Encapsulation and scintillation involves the introduction of new chemicals or other particles to the systems. The interaction of these materials may not only interfere with the hydrodynamics of the system, but also could have a direct impact on the reaction rate. Electrical methods such as the Coulter counter technique require the continuous phase to be moderately conductive. As such, this technique was used only in situations where the continuous phase was aqueous (Sprow, 1967; Narsimhan et al, 1980). It would be unlikely that the continuous phase of the present system has the required electrical conductance. Light transmittance and light scattering techniques were found to be able to produce rapid results. With the light transmittance technique, signal analysis is very rapid, but calibration using another method such as photography is necessary (Godfrey et al, 1994). Thus some of the convenience of the technique is lost. Light scattering techniques such as the Phase Doppler anemometry were successfully employed for dispersions at extremely low concentrations, $\phi = 0.002$ (Willie et al, 2001) and $\phi < 0.0003$ (Zhou and Kresta, 1998b) which is far below the requirement of the present study.

Indirect methods such as those mentioned above do not provide absolute drop size distribution as the photographic technique (Skellan and Moeti, 1990). McLaughin and Rushton (1973) considers the photographic techniques to be the most accurate methods of measurement. In addition, photographic methods were selected for systems with a relatively high continuous phase viscosity (Shimizu et al, 1999; Stamatoudis and Tavlarides, 1985). Therefore it has been decided that employing a photographic technique would be most suitable for the present investigation.

### 3.3.1 Selection of the Photographic Technique

There are numerous arrangements of photography that have been used for drop size measurement including techniques such as photography through the vessel wall, photographic probe and microscopic photography. As there have not been any previous drop
size studies for the present system, attempts were made to measure the drop sizes using several arrangements such as measuring cell, photographic probe and microscopic photography.

3.3.1.1 Measuring Cell

Preliminary tests were conducted using an arrangement similar to that used by Ban et al (2002), where photographs were taken through a measuring cell. The objective of this technique was to withdraw samples from the stirred tank to a measuring cell through a sampling tube, obtain the images of the contents in the cell and then recycle them back to the tank. A rectangular cell with the dimensions of $10 \times 15 \times 0.5$ mm was constructed from glass. The sides of the cell were blackened with cardboard to minimise the light from unwanted sources. In the initial stages, withdrawal system was not used since it is important to determine whether it is possible to obtain reasonable images through the cell. Liquid-liquid dispersion was prepared as described above in section 3.2.1 and samples were withdrawn 15 min after the commencement of the run and were transferred to the cell. Images were taken using a Sony video camera (CCD-TRV 16E) with the light source (100W flash light) placed on the opposite sides of the cell. The video camera was connected to a PC with image analysis software, Image Pro Plus. Software allowed a snapshot of the video image to be taken (Figure 3.7 (a)).

![Figure 3.7: Image taken through the (a) measuring cell arrangement (b) video probe arrangement.](image-url)
3.3.1.2 Photographic Probe

Photographic probes have been used for drop size measurements in numerous studies. Earlier examples of the arrangement were such that lighting and photography was achieved by using two separate probes (Stamatoudis and Tavlarides, 1985; Okufi et al., 1990; Pacek and Nienow, 1995). In later developments, the arrangement consisted of integrated lighting system, thus only one probe was employed in the dispersion (Ritter and Kraume, 2000; Schulze et al., 2000; Kraume et al., 2004; Gallego-Lizon et al., 2000). A probe with integrated lighting was also used to conduct preliminary tests for the present system. However, in the present case, the CCD camera was fixed at the bottom of the probe. This caused the size of the probe to be significantly larger than the endoscopic probes used in previous studies. The camera shutter frequency was synchronized with that of a high-energy strobe light. Images from the camera were relayed to a PC containing image analysis software. Snapshot of the video image taken with the arrangement is shown in Figure 3.7 (b).

3.3.1.3 Microscopic Photography

The third photographic method used in the present work employed a microscope (Pulpix TMC-76). This method involved the samples to be transferred to a laboratory watch glass and observed through the microscope. The microscope unit contained a video port which enabled the images to be relayed to and viewed on a PC. The image analysis software allowed snapshot of the magnified image to be taken. Dispersion was prepared as described in section 3.2.1. A sample was taken after 15 min of agitation and few drops were placed on the watch glass placed under the microscope. The microscopic unit contained an internal light source, but this did not assist in the production of clear images. This was resolved by the use an external light source. Schott Mainz KL 150B endoscopic light provided suitable lighting to produce clear images. An example of the image obtained by this arrangement is shown in Figure 3.8.
Comparing the images produced by the three techniques, it is apparent that only the images obtained from the microscopic technique has sufficient quality and magnification for accurate drop size measurement. It is also advantageous due to the small volume of sample required in the microscopic technique compared to the measuring cell arrangement. In addition, unlike the video probe arrangement, errors arising from hydrodynamic disturbance is also minimal. Considering the advantages of the microscopic technique, it would the most appropriate choice for the present study. It should also be noted that although the chosen technique was the simplest compared to various sophisticated methods available for drop size measurement, the photography and sample removal being the most-used technique in recent publications (Godfrey and Slater, 1994).

### 3.3.2 Experimental Procedure for Drop Size Measurement

The experimental run commenced with the instantaneous addition of MEA. Details of preparation of the continuous phase and reactor setup are given in section 3.2.1. All drop size measurements were carried out at a constant temperature of 20 °C. Samples were withdrawn using disposable serological pipettes. The inside diameter of the pipette was 2.7 mm which is several times larger than the largest drop. This ensured that drops of all sizes were sampled. At the given sample time, the pipette was immersed into the dispersion at the predetermined sampling location (Figure 3.5). Suction was applied at a rate whereby the likelihood of drop coalescence was minimal. The rate cannot be too low because the drops
will coalesce at the entrance of the pipette tip (Hocq et al, 1994). Since uniform and 'quasi-laminar' flow of each drop in the pipette may prevent collision of drops (Ban et al, 2002) a constant rate of suction was applied during the sample withdrawal process.

Several drops from the sample were then placed on a laboratory watch glass (50 mm in diameter). Number of drops required for obtaining statistically valid distribution was estimated to be 300 drops. This number was a compromise between statistical demand on the accuracy of the drop size distribution and the time required for measurement (averaging 20 minutes for 300 drops). 300 drops would lead to a maximum error of 3% in the measured Sauter mean diameter (Giles et al, 1971). Ritter et al (2000) found that the cumulative drop size distribution did not show significant difference when the number of drops increased from 200 to 600.

Prior to the addition of a sample, the watch glass was placed on the microscope which magnified the images to $\times 200$. The endoscopic light source was turned on and manoeuvred in a manner such that the light shone directly on the centre of the watch glass. The image analysis software, Image Pro Plus, allowed the images under the microscope to appear on the computer screen as a video image. Then a photographic snapshot of the video image was taken and saved as a JPEG image file. It should be noted that the image appeared on the computer screen was confined to a specific region on the watch glass. Horizontal movement of a platform on the microscope unit allowed other regions to be viewed. Ensuring that no drop would be repeatedly photographed, the platform was moved only in one direction. Number of images photographed was such that they contained at least 300 measurable drops. Measurable drops were only those reasonably in-focus an image and spherical in shape. The whole process took approximately 1 to 10 minutes depending on the number of image snapshots taken.

Initially there was a concern over the time lapse between the sample withdrawal and photography. There was a possibility that drops would coalesce and/or reaction may take place during the process, which would compromise the accuracy of the measured drop sizes. Tests were carried out to determine whether drops exhibited changes in size whilst on the watch glass. Observation of the drop through the microscope did not show any significant movement within the viscous continuous phase hence coalescence was unlikely to occur. After the period of time however, the dispersed phase (higher density) tended to settle to the
bottom of the watch glass. To obtain statistical information on coalescence effects, drop sizes were measured immediately after withdrawal and at regular intervals thereafter. It was found that $d_{32}$ values varied ±4% after period of 25 minutes and ±7% after 60 minutes. Drop size distribution of the sample also showed a slight shift towards larger drop sizes with time, indicating of coalescence. In general, the effect of the coalescence was minimal and is unlikely to be a major source error in the duration of photographic process which was within 10 minutes in all cases.

Once sufficient number of image snapshots has been taken, the droplets in the images were measured using the image analysis software. Given that the images have been magnified some form of calibration was required. The Image Pro software allowed this by assigning a length unit to the pixel size in the image (an image contained 720 by 568 pixels). The calibration was conducted using a 1 mm graticule with 0.1mm markings supplied with the microscope unit which in turn was verified by calibration tape with graticule of 500µm. Once the unit of actual length unit was associated with pixel sizes, the relationship was stored and used to determine the actual size of droplets.

Commercial software packages such as Image Pro Plus have the capability to analyse images and measure drop sizes automatically. The ability to automate the drop sizing process depends largely on the quality of images and the software packages ability to identify contours of each drop. Most software packages allow enhancement of contrast and colour (Pacek et al, 1994). Even with the enhancement features, the limited resolution, difference in brightness through reflection and the overlapping contours of drops make automated determination of drop sizes very difficult. Ritter and Kraume (2000) found that automated sizing had high failure rates. Thus many have resorted to using manual or semiautomatic measurement of droplets in liquid-liquid dispersions (Pacek et al 1994; Ritter and Kraume, 2000; Schulze et al, 2000; Gallego-Lizon et al, 2000; Kraume et al, 2004). This process is extremely time consuming, but generally considered essential for producing accurate results (Paul et al, 2004). In the present investigation, the quality of the images, both in terms of contrast and high proportion of overlapping drops, meant that automated measurement was unfeasible. Thus manual measurement was used for all experiments. Manual measurement was conducted by simply placing the cursor at two opposite ends of the droplet. The software determined the number of pixels between the two cursor points and using the stored
calibration, a unit length was expressed in terms of microns. Then drop diameter values were exported directly to Microsoft Excel for analysis.

Initial sample was withdrawn 5 minutes after the addition of the dispersed phase to the system. Further samples were taken at 10, 15, 20, 30, 40, 60, 90, 120 minutes and every hour thereafter until the experimental run was stopped after 5 hours. It was apparent from droplet images that the dispersion became cloudy initially and drop sizes could only be measured after a certain proportion of the dispersed phase has reacted. In the case of the Rushton turbine impeller operating at 150 rpm, measurable drops only appeared after 30 minutes of agitation. Whilst at higher speeds or when marine propeller was employed, drops were measurable at earlier sample times. Given that the present system was reactive, the dispersed phase progressively disappeared with time and this coincided with number of the drops appearing in each image snapshot. For instance when Rushton turbine was operating at 600 rpm, only 6 to 8 images were required to obtain 300 measurable drops at the sample time of 5 minutes. On the other hand, the number was closer to 100 images at 60 minutes when virtually all of the dispersed phase had reacted. Thus it was decided that experimental run would be prematurely stopped at the point where the number of images required to obtain 300 measurable drops exceeds 100. Due to these factor factors, the number of samples taken for each experimental runs varied. Number of samples taken ranged between 6 and 11 for each experimental run. Therefore number of drops measured in each experimental run also varied from 1800 to over 3300. Table 3.4 lists the experiments in which drop size measurements were carried out.

<table>
<thead>
<tr>
<th>Impeller type</th>
<th>Rushton Turbine</th>
<th>Propeller</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersed phase volume fraction</td>
<td>0.028</td>
<td>0.02</td>
</tr>
<tr>
<td>Impeller speed (rpm)</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>350</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>450</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td></td>
</tr>
</tbody>
</table>
An attempt was made to conduct the experiments at the dispersed phase volume fraction of 0.035, but was found to be unsuccessful. The dispersion remained cloudy throughout the experimental run and the contrast between the dispersed and the continuous phase was insufficient for drop measurement. Thus it appears that the drop size measurement technique is limited to cases where the dispersed phase volume fraction is below 0.028.

3.4 Reactant Concentration Measurement

In analysis of chemical reactions, measurements are made under dynamic conditions in which the concentration of reactants and products are changing as a function of time (Skoog, 2004). There are numerous techniques that have been used for such analysis, including classical methods such as titrimetric and gravimetric, electrochemical methods, spectrochemical and chromatographic methods. The applicability of these methods depends on the physical and chemical properties of the reactive system.

Present system involves the reaction of monoethanolamine (MEA) and polysiobutylene succinic anhydride (PIBSA) to produce an emulsifier (ester and amide derivatives). To the author’s best knowledge, no study of the kinetics of the system has been published in the open literature. However, there has been some chemical analysis conducted examining certain aspects of the system under investigation. Ghaicha et al (1993) investigated the effect of the emulsifier (ester derivative) and its monolayer interaction with water-ammonium nitrate. The qualitative chemical interactions were examined using a FTIR instrument with a KBr beam splitter. Experiments were such that concentration of the emulsifier varied with each analysis. It was found that at low concentrations, the peak intensities were extremely weak which made it difficult to draw any meaningful conclusions.

There were a number of studies that characterised some component of the present system. Reynolds et al’s (2003) investigation involved the examination of the purity of the product formed during the reaction by using FTIR, $^1$H and $^{13}$C NMR. Completion of the reaction between PIBSA and polyethylene glycol was verified with FTIR and $^1$H NMR (Al-Sabagh and Atta, 1999). Products and reactants involved in the reaction between PIBSA and amine terminated nitrile rubber (ANTBAR) were analysed by a FTIR technique (Chung et al,
1988). Tomlinson et al (1997) characterised the surfactant produced in the reaction between PIBSA and various polyamines using UV, IR and $^1$H NMR spectroscopy. The studies mentioned above were all qualitative. However, Papke et al (1991) used FTIR to quantitatively measure interaction between basic calcium alkaryl sulfonate dispersion and a surfactant produced in the reaction between PIBSA and triethylenetetraaine. In contrast to the system investigated in this project, Papke’s system did not involve a reaction. Despite these differences, some analogies can be drawn to assist in the development of a chemical analysis technique for the present study. Based on the literature information on the chemical analysis of constituents in the system, spectroscopic method should be considered as means of determining the reaction rates. Therefore, preliminary tests were conducted using nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy.

### 3.4.1 Selection of Analysis Technique

#### 3.4.1.1 NMR

Preliminary tests were conducted using pure samples of the reactants and the products in the system. Proton or $^1$H NMR was conducted using the Bruker VSP 300 Pulsed Fourier Transform NMR spectrometer operating at 300 MHz. All samples were dissolved in deuterated chloroform (CDCl$_3$). MEA spectrum showed intense triplets at approximately 3.0 ppm and 2.2 ppm. PIBSA contained some hydrogens giving complicated splitting patterns in the region between 1.5 ppm and 1.0 ppm. The matrix of intense peaks in the product were virtually the same as those of the PIBSA spectrum. However, their intensities relative to others varied slightly. Intense peaks that were observed in the MEA spectrum did not appear in the product $^1$H NMR spectrum (see Appendix A.2 for all spectra). In general, an intense peak specific to a component in the reaction could not be isolated. The preliminary tests indicated that NMR would be unsuitable to determine the reaction rates for the present system. Further testing and spectral analysis may have produced improved results, but parallel testing conducted using FTIR showed more promise. In addition, FTIR was found to be less expensive and required less time in terms of sample preparation and analysis than NMR. Thus NMR testing was ceased and FTIR was ultimately chosen as the technique for the quantitative analysis. The following sections detail the development of FTIR to determine the reaction rates of the PIBSA and MEA reaction.
3.4.1.2 FTIR

A great advantage of FTIR spectroscopy is that virtually any sample in any state can be studied. Liquids, solutions, pastes, powders, films, fibres, gasses and surfaces can all be examined by this judicious technique. High spectral signal-to-noise ratio can be obtained from modern instrumental analysis which allows the detection of constituents present in very low concentrations and subtle differences between and among multi constituent specimens (Ghauch et al, 2006). Over the years there have been numerous and ever increasing utilisation of FTIR for quantitative purposes (Chiou et al, 1997; Dimitrakopoulos et al, 1996; Storey et al, 1998; Xu et al, 2000; Scott et al, 2003).

In the present investigation, the substance to be tested is in liquid form and the most obvious infrared technique would be transmission spectroscopy with samples held in liquid sampling or solution cell. Transmission spectroscopy is the oldest and most basic infrared method (Stuart et al, 1998). Use of liquid solution cell for quantitative analysis can be considered to be simplest of all FTIR sampling procedures (Williams et al, 1995). The liquid solution is sandwiched between large crystals (the windows) positioned such that the IR beam from the interferometer passes directly through the assembly from one window, through the sample, and then through the other window to the detector, as illustrated by Figure 3.9.

![Figure 3.9: Liquid sampling cell placed in the path of the IR beam (Kenkel et al, 2003).](image-url)
3.4.2 Quantitative Analysis Using FTIR

Quantitative analysis using transmission involves several steps:

- Choosing sample cell
- Selecting analyte band
- Choosing solvent
- Obtain a calibration plot
- Determine the concentration of analyte

3.4.2.1 Choice of Sample or Solution Cell

A variety of solution cells differing in design, optical window material, pathlength and internal volume are available. The selection of cell is a compromise between availability, cost and functionality (Gallignani, 2004). Considering all these aspects a solution cell with the following specification was selected:

- Window material: NaCl
- Pathlength: 50 µm
- Type: permanently sealed
- Geometry: rectangular

Figure 3.10: IR solution cells used in the analysis (Gallignani, 2004).
3.4.2.2 Choosing a Suitable Analyte Band

First step in the quantitative procedure is the identification of the main components of that constitutes a sample. A sample generally consists of the reactants, PIBSA and MEA, the diluent, mineral oil and the product (various derivatives of the emulsifier). Each of these components has absorption bands that would be present in an FTIR spectrum. Firstly, it will be useful to identify which are the characteristic bands of each component. Stuart (1998) suggests that liquid films provide a quick method for examination of liquid samples.

Initial tests were conducted by placing a sample of pure components between two KBr (potassium bromide) disks. Spectral range of 400-4000 cm\(^{-1}\) was chosen. Spectra of each component in the sample are shown in Appendix A.3. MEA spectrum showed distinct absorption peaks at around 3000 cm\(^{-1}\). According to Pavia \textit{et al} (2001), this is a characteristic of asymmetric and symmetric stretching of C-H bonds. N-H stretching band can generally be found in the range of 3500-3000 cm\(^{-1}\) and O-H stretching vibration at the range from 3400-3300 cm\(^{-1}\). These bands were not easily found in the spectra, possibly because they could be overlapped by strong C-H stretching bands. Some of the sharp peaks present below 1500 cm\(^{-1}\) may be due to associated bending modes of the methyl groups where CH\(_2\) and CH\(_3\) bending generally show absorption peaks at 1465 cm\(^{-1}\) and 1375 cm\(^{-1}\) respectively. There are several other weaker peaks below 1600 cm\(^{-1}\) possibly due to bonds associated with alcohol and amine functional groups in MEA. The spectrum for the mineral oil shows some sharp peaks around 3000 cm\(^{-1}\) and below 1500 cm\(^{-1}\). They are associated with C-H stretching and bending modes similar to those in MEA.

PIBSA spectrum also contained distinct peaks associated with C-H stretching and bending modes. Numerous smaller peaks were also present below 1500 cm\(^{-1}\). It is difficult to identify the vibrational modes associated with some of these peaks due to their relatively low absorption intensity and interference from neighbouring peaks. However, there were two clear and distinct peaks at 1864 cm\(^{-1}\) and 1788 cm\(^{-1}\). Pavia \textit{et al} (2001), suggests that five-membered ring anhydrides have bands near 1860 cm\(^{-1}\) and 1780cm\(^{-1}\), which are associated with symmetric and asymmetric stretching modes of the carbonyl group (C=O). Several studies have produced FTIR spectra of PIBSA and the anhydride absorption peaks were found to be in same frequency as those found in the present investigation (Chung and Hamed, 1988; Ghaicha \textit{et al}, 1993; Al-Sabagh and Atta, 1999; Harrison \textit{et al}, 2002).
A spectrum of the product in the reaction between PIBSA and MEA was also obtained. Pure products were prepared by conducting an experimental run similar to drop size measurement experiment run. The continuous phase contained 56/44 vol % PIBSA/oil and MEA was added so that its volume fraction in the mixture was 0.028. Rushton turbine impeller was operated at 350 rpm for 1 hour from the commencement of the reaction. This was considered to be a sufficient time for bulk of the PIBSA and MEA to be converted into products. Thereafter, the impeller speed was increased to 700 rpm for a further period of 1 hour allowing the reaction to achieve complete conversion.

The product mixture is expected to contain several compounds: all of the mineral oil, the emulsifier (mixed ester/amide derivatives), unreacted PIBSA and/or MEA. In addition, some impurities such as the imide derivative and the product of the reaction between MEA and hydrolysed PIBSA may also be present in small quantities. The spectrum contained the expected strong C-H stretching band at 3000 cm\(^{-1}\) and C-H bending modes in region below 1500 cm\(^{-1}\). These bonds are present in all of the components in the products mixture. The anhydride peaks at 1864 cm\(^{-1}\) and 1788 cm\(^{-1}\) have completely disappeared indicating that all of the PIBSA that can be detected in the FTIR have reacted. Three new peaks at approximately 1740 cm\(^{-1}\), 1645 cm\(^{-1}\) and 1565 cm\(^{-1}\) were present. One of the most characteristic features in the spectrum of a normal ester is the strong C=O which appear in the range from 1750 to 1735 cm\(^{-1}\) (Pavia et al, 2001). When it is conjugated to a C=C or a phenyl group, the C=O stretching vibration is expected to shift the band to lower frequencies by about 15-25 cm\(^{-1}\). Given that peak in the spectra is within this range, the peak at 1740 cm\(^{-1}\) can be attributed to ester derivative emulsifier. However, there's a possibility that the peak is associated with carboxylic acid group in the amide derivative emulsifier where C=O bond stretching of the acid group is expected to produce a peak at 1730-1700 cm\(^{-1}\). But the carboxylic acid band is expected to shift to lower frequencies with the conjugation. Primary and secondary amides have broad C=O absorption in the range from 1680 cm\(^{-1}\) to 1630 cm\(^{-1}\). The C=O band partially overlaps the N-H bending band which appears in the range 1640-1620 cm\(^{-1}\), making the C=O band appear as a doublet (Pavia et al, 2001). Thus it is reasonable to assume that the peak that appears at 1645 cm\(^{-1}\) in the product spectra is attributed to the amide derivative emulsifier. The peak at 1565 cm\(^{-1}\) can be associated with acid/salt (amino acid existing as zwitterions internal salt) group in the ester derivative emulsifier. Acid/salt groups exhibit spectra combination of carboxylate and primary amine
salt where N-H of amine salts bending absorption occurs at range from 1610 cm\(^{-1}\) and 1550 cm\(^{-1}\), whilst carboxylate salt C=O asymmetric stretching mode occur near 1600 cm\(^{-1}\) (Pavia \textit{et al.}, 2001). The impurity, imide derivative normally show strong absorbance for C=O stretching at 1770 cm\(^{-1}\) (Ghaicha \textit{et al.}, 1993). Absence of such peak suggests that FTIR traceable amounts of imides weren’t present in the product mixture.

Examination of spectra of all the components gives a good indication of the band/s that could be chosen for quantitative analysis. To determine the conversion rate, one must to choose band/s that is solely associated with either the reactants or the products. If this is not the case, it wouldn’t be possible to relate absorbance intensity of the band/s to the concentration of a specific component. For instance, absorption bands at 3000 cm\(^{-1}\) are attributed to C-H stretching which is the bond present in both reactants and products, hence cannot be used for quantitative analysis. Similarly, bands below 1500 cm\(^{-1}\) should not be used.

Anhydride peaks associated with C=O stretching at 1788 cm\(^{-1}\) and 1864 cm\(^{-1}\) only appears with the presence of PIBSA, but disappears as the reaction proceeds and thus can be related to conversion. Similarly product bands of ester, amide and acid/salt which have peaks at 1740 cm\(^{-1}\), 1645 cm\(^{-1}\) and 1565 cm\(^{-1}\) can be directly related to the concentration of products. Therefore, it is possible to follow the reaction by the disappearance of anhydride peaks or the appearance of amide, ester, and acid/salt peaks. However, the spectral bands presented so far have been solvent-free and their intensities and frequencies may vary with the presence of a solvent.

\textbf{3.4.2.3 Choice of Solvent}

As discussed in earlier sections of this chapter, present system contains quite viscous components. The mixture containing reactants (PIBSA and MEA), mineral oil and products could reach a viscosity as high as 12 Pas. As a consequence the mixture cannot flow easily through the narrow path within the solution cell. Therefore a solvent is required to dilute the solution. There are number of factors that must be considered when choosing a solvent. Firstly, solvents such as ethanol and methanol cannot be used as they are not compatible NaCl with window. Alcohol or water constituents in these solvents leads to damage to the NaCl window of the solution cell. In addition, the solvent must be capable of dissolving the mixture. Toluene, dichloromethane and chloroform are commonly used solvents and
therefore they were tested for their dissolving properties. Small amount samples were withdrawn during an experimental run and added to a viol containing each solvent. Solubility of the sample in the solvent was examined by visual inspection. Chloroform and dichloromethane readily dissolved the sample with virtually no shaking. Toluene also dissolved sample fairly easily, but with some agitation. Thus it was apparent that chloroform and dichloromethane had slightly better dissolving properties than toluene, but all three were deemed to be suitable in term of their dissolving properties.

One of requirements of quantitative measurement would be to locate an isolated band of the analyte and extract the relevant intensity information by peak height or peak area (Coates, 2002). When a solution is tested, both analyte and solvent absorption bands will be present in the spectra. It is useful to choose a solvent which contains absorption bands that do not interfere with the band/s chosen for quantitative analysis. Potentially useful bands for quantitative analysis were all in the region of 1900 – 1500 cm\(^{-1}\). FTIR tests were conducted to determine the frequency of the bands characterising each of the solvents. The spectra of each solvent and the components in the mixture in the useful region of 1900-1500 cm\(^{-1}\) is shown in Figure 3.11.

![Figure 3.11: Spectrum of pure solvents and components with quantifiable analyte bands in the region (1900-1500 cm\(^{-1}\)).](image-url)
The IR spectrum for each solvent shows varying numbers of bands in the frequency region of interest. Toluene contains numerous bands in the region and these are more than likely to interfere with those bands to be used for quantitative analysis. Therefore this should was disregarded as a potential solvent. Dichloromethane contains one relatively small peak at 1735 cm\(^{-1}\) and a peak at 1525 cm\(^{-1}\) characterises IR spectrum for chloroform. Considering the peaks to be used for quantitative analysis, the band characterising dichloromethane is in close proximity to ester peak and may also interfere with the anhydride peak at 1788 cm\(^{-1}\), whereas the band representing chloroform is likely to interfere only with the acid/salt peak at 1565 cm\(^{-1}\). Based on these observations, chloroform was deemed to cause the least interference and hence was chosen as the solvent. A dilution ratio of 1/5 (w/w) was enough to readily dissolve the sample and was also able to reduce the viscosity of the solution to a manageable level. Stuart et al (1998) suggested that for quantitative analysis, solution cell with a pathlength of 50 µm should contain sample concentration of at least 10%. The dilution ratio of 1/5 (w/w) falls well within the range recommended and therefore was chosen as the dilution factor for all samples.

### 3.4.2.4 Calibration Procedure

Traditionally, quantitative analysis is carried out by constructing a calibration curve of absorbance versus concentration and then measuring the unknown concentration of a given sample by using either the absorbance peak or absorbance area (Koenig, 1992). The process of concentration determination can be divided into several steps:

- Preparation of solutions of known concentrations (standard solutions)
- Choosing a suitable absorption peak
- Obtain absorption data of the chosen peak
- Plot a calibration curve
- Obtain absorption data (of the chosen peak) of for the sample with unknown concentration
- Use the calibration curve to determine their concentration
1) Preparation of standard solutions

First step in the calibration procedure is to record the spectra of a series of prepared samples with known concentrations/compositions (Coates, 2002). Series of standard solutions were prepared by mixing known amount of the products with specific quantity of the continuous phase (PIBSA/oil mixture). Pure products were prepared using the procedure described in section 3.4.2.2. The purity of the product was tested by placing a sample between KBr disks. The complete disappearance of the anhydride peaks suggested that PIBSA had been completely converted. Continuous phase containing 56/44 vol% PIBSA/oil was prepared by as per standard experimental procedure detailed in section 3.2.1.

- 500 ml of pure PIBSA/oil mixture was transferred to the fully baffled mixing vessel. Agitation was started and continued for 10 minutes. Approximately 2.5 ml sample was withdrawn using an electronic pipetter with 10 ml pipette tip attachment.

- The sample was transferred to a viol and weighed using electronic balance. Given the mixture was quite viscous, significant quantity of the sample remained entrapped within wall of the pipette tip. Thus the actual amount of sample in the viol was about 1.5-2.0 ml.

- The volume of solvent (chloroform) required to maintain a dilution of 1/5 (w/w) was calculated and added to the viol. Liquids in the viol were mixed to ensure homogeneity was achieved. The viol was labelled and stored for FTIR analysis.

- Measured quantity of 50 ml of pure product mixture was slowly added to the liquid in the mixing vessel. The mixture was agitated for 10-15 minutes until homogeneity was achieved. Then a sample of 2.5 ml was withdrawn from the mixture, weighed and diluted in the same manner as mentioned above.

- Thereafter, incremental amounts of product mixture was added to the liquid in the vessel and samples were taken. Table 3.5 shows the incremental volumes of product mixture added and respective volume fraction of PIBSA in the mixture.
Table 3.5: The series of samples taken for calibration

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Total volume of pure product added to the PIBSA/Oil mixture</th>
<th>PIBSA volume Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>0.55</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>0.50</td>
</tr>
<tr>
<td>3</td>
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</tr>
<tr>
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<tr>
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<td>0.18</td>
</tr>
<tr>
<td>9</td>
<td>1500</td>
<td>0.14</td>
</tr>
</tbody>
</table>

2) FTIR analysis of standard solutions

As discussed in section 3.4.2.1, NaCl solution cell with a 50 µm pathlength was used for the analysis. Perkin-Elmer 1725X Fourier transform infrared spectrometer with MTC detector (cooled by liquid nitrogen) was used for the chemical analysis (Figure 3.12). Spectral analysis was conducted using the software, *Spectrum for Windows 2.0*.

![FTIR spectrometer](image)

Figure 3.12: FTIR spectrometer used in the investigation.
The data acquisition parameters were defined such that the spectral range was set from 4000 cm\(^{-1}\) to 400 cm\(^{-1}\) which contained the spectral region of interest, 1900-1500 cm\(^{-1}\). The instrument was set to produce 16 scans per spectrum with 8 cm\(^{-1}\) nominal resolution and at 2 cm\(^{-1}\) intervals. Samples were transferred and removed from the solution cell using Luer tipped syringe. The analysis was conducted using standard FTIR laboratory procedure where background scan was conducted prior to the scanning of the cell containing a sample. Once the spectral data was obtained and saved for analysis. All the standard solutions were analysed in the same manner and a series of spectra was obtained for the calibration plot.

3) **Calibration plot**

First step in obtaining a calibration plot was to choose a suitable analyte band. The bands that can be used for quantitative analysis are the PIBSA anhydride peaks at 1788 cm\(^{-1}\) and 1864 cm\(^{-1}\) and the product peaks at 1740 cm\(^{-1}\) (ester) 1645 cm\(^{-1}\) (amide) and 1565 cm\(^{-1}\) (acid/salt). Stuart (1998) suggested that for the technique to be sensitive a band with an intense peak must be chosen. The peak needs to be isolated in a manner such that there is essentially no overlap of the analytical absorption band.

Previous research on quantitative analysis also produced matrix of FTIR spectral bands similar to those obtained in the present investigation (Dimitrakopoulos *et al.*, 1996; Krishnan *et al.*, 2000). The spectra obtained in both investigations contained anhydride reactant peaks and amide and acid product peaks at similar frequencies. Dimitrakopoulos *et al* (1996) monitored the integrated intensity of the amide band to determine the amadisation reaction rate involving PMDA and ODA. The anhydride peaks were the most intensive, and thus the effect of noise was deemed to be negligible. As such anhydride bands were successfully used to monitor the anhydride concentration with time. Krishnan *et al* (2000) investigation produced FTIR spectra in which aminolysis reaction rates could be determined by monitoring the reactant (anhydride) and/or product (amide/acid) peaks. Amide formation was deemed to be too difficult to monitor because of high reactant concentration resulting in product precipitation. Therefore, ammonolysis rate was determined using the anhydride peak loss with time.
In the present case, anhydride peak at 1788 cm\(^{-1}\) is clearly the most intensive and to a great extent is isolated from neighbouring bands. Also given the precedent of its successful use to monitor reactions, anhydride peak at 1788 cm\(^{-1}\) is an obvious choice to monitor the reaction between PIBSA and MEA.

The next step would be to correlate the intensity of the selected band with the concentration of the analyte (in this case PIBSA). Using just the peak height with no other reference point is generally not recommended. This is because the influence of any underlying background is unknown and this can be dependent on several experimental factors, such as the impact of neighbouring absorption, scattering, reflection effects and refractive index phenomena (Coates, 2002). These errors can originate from both the sample and the sample handling method and/or accessory. To reduce some of these sources of error, some form of baseline correction is required. Various studies have used different baseline correction methods according the environment surrounding the selected analyte band/s. Schrader (1995) detailed some of the baseline correction methods that can be used for spectral analysis.

The final choice of method for determining the analyte absorbance intensity including, peak height or area and the specific baseline line correction method is determined by what method provides the best fit and is most reproducible (Coates, 2002). In the present system, peak height with single-point baseline correction at 1822 cm\(^{-1}\) was deemed to be the most reasonable choice to determine the absorbance intensity of the selected band (anhydride peak at 1788 cm\(^{-1}\)). Once the choice was made, calibration curve was constructed using the selected band data.
The calibration curve shown in Figure 3.13 correlates the intensity absorbance with the volume fraction of PIBSA in the system. In an ideal situation, a linear plot is obtained, indicating Beer’s law is being obeyed. Deviations can be due to a number of different factors ranging from sample to instrumental effects (Coates, 2002). In this particular case, the calibration curve does not show a linear relationship below a certain volume fraction and the calibration line does not intercept at zero. However, this is not necessarily a problem if the measurement conditions are reproducible (Coates, 2002). Correlation coefficient, R, is an indication of the agreement between the data set to the calibration model. A “good” calibration will achieve a value of $R^2$ between 0.90 and 0.95, whereas a “superior” calibration may attain a value of 0.98-0.99 or even higher (Mark, 2002). In the present case $R^2$ (coefficient of determination) value is 0.98, which is an indication of good agreement between the calibration curve and the data set.

3.4.2.5 Determination of PIBSA Concentration

Firstly, the continuous phase was prepared in the same manner as was done for the drop size experiments. Prior to the addition of the dispersed phase MEA, the sample viols were kept ready. There was a time lapse between sample withdrawal from the reactor and FTIR
analysis. It was possible that MEA will react with PIBSA at room temperature even without agitation. This was tested by the addition of MEA to a standard PIBSA/oil mixture at room temperature. After a period of time, there was a slight temperature increase indicating that the reaction did proceed even without agitation. Therefore, it was necessary that samples needed to be kept at low temperature to inhibit the progression of reaction until FTIR analysis was conducted. Combination of ice bath and refrigeration was utilised to achieve this. The ice bath was prepared by placing a layer of crushed ice and a small quantity of water in a container. Salt was added to reduce to melting point of the mixture. The temperature of the bath was maintained below 2 °C with the continual addition crushed ice.

The empty sample viols used to retain withdrawn samples were placed in the ice bath. Keeping the viol at low temperature assisted in decreasing the temperature of samples, thus stopping the reaction. Water bath was employed to maintain the reactor temperature at 20 °C. Samples were taken at regular intervals until the end of the experimental run, which was 5 hours after the commencement of the reaction. After the completion of the run, the viols containing the samples were taken from the ice bath and were refrigerated below 5 °C for FTIR analysis. Withdrawal and analysis of the samples with unknown concentrations were conducted using a procedure that was similar to the one used for standard solutions. The absorbance intensity values were determined by using single-point baseline corrected peak height at 1788 cm\(^{-1}\). These values were then interpolated from the calibration plot to give the corresponding concentration of PIBSA. Table 3.6 lists the reaction experiments that were conducted during this investigation.

**Table 3.6: Reaction experiments conducted**

<table>
<thead>
<tr>
<th>Impeller type</th>
<th>Rushton Turbine</th>
<th>Propeller</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersed phase volume fraction</td>
<td>0.028</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>Impeller speed (rpm)</td>
<td>350</td>
<td>350</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td></td>
</tr>
<tr>
<td></td>
<td>600</td>
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</tbody>
</table>
3.5 Viscosity Measurement

All rheological measurements were conducted using Carri-Med CSL 100 rheometer with parallel plate arrangement. The instrument was fitted with an IEEE488 interface which enabled the instrument to be controlled by a computer. Air bearing support for all rotating parts ensures frictional effects are minimised. The instrument had the capacity to apply a shear stress ranging from $0.008$ to $2.54 \times 10^4$ Pa. Depending on the geometry and technique, viscosities in the range of $5 \times 10^{-5}$ to $2.5 \times 10^{10}$ Pa.s could be determined. The hard chrome plated copper bottom plate equipped with a Pt100 controlled Peltier system is used for temperature control. Standard fluid circulating through the Peltier system allows samples to be tested at a range from 5 to 80ºC with a stability and accuracy of $\pm 0.1$ºC.

3.5.1 Raw Materials

Viscosities of raw materials were tested using shear stress sweep as the mode of operation. The mode was such that a linearly incremental increase of shear stresses (within a selected range) was applied within a set time. Preliminary tests showed that all raw materials in present investigation were Newtonian and as such more sophisticated mode of operation was not necessary. All viscosity tests were conducted using the standard experimental procedure for parallel plate arrangement, namely in Carri-Med CSL instruments. MEA, PIBSA and mineral oil were tested at the temperature of 20 ºC. In addition, the viscosity PIBSA and mineral was obtained for a range of temperatures.

3.5.2 Dispersion

There were some concerns with using a rotation viscometer for viscosity measurement of the reactive dispersion. It was likely that applied shear stress (with the rotation of the upper plate) to a sample would lead to the progression of the reaction during the test. Thus the composition of the sample was unlikely to remain constant throughout the testing period. Preliminary tests showed that this did occur, as indicated by the increase in viscosity with progression of the test. One may suggest that this was shear thickening behaviour of the dispersion, but this phenomenon only occurred at early sample times, when much of the
mixture remained unreacted. Alternative means of viscosity measurement was possibly less advantages. Compared to other techniques this arrangement required only a small sample volume. Removal of large volumes would result in significant disturbance to the hydrodynamic of the reactor. Simplicity and speed at which test can be conducted is also advantageous, especially given the reactive nature of the system. Therefore, parallel plate arrangement was selected as the method for viscosity measurement of the dispersion. Shear stress sweep operation mode with stress range of 100-500 Pa was selected. Measuring system consisted of 2cm plate with a 1000µm gap size. Samples were withdrawn using disposable pipette (same as those used in drop size studies) from the sampling region highlighted in Figure 3.5. In addition samples times and series of experiments conducted (Table 3.7) also reflected those of the drop size studies.

Table 3.7: Viscosity tests conducted.

<table>
<thead>
<tr>
<th>Impeller type</th>
<th>Rushton Turbine</th>
<th>Propeller</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersed phase volume fraction</td>
<td>0.028</td>
<td>0.02</td>
</tr>
<tr>
<td>Impeller speed (rpm)</td>
<td>150</td>
<td>150</td>
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<tr>
<td></td>
<td>200</td>
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<td>450</td>
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<td></td>
<td>600</td>
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</tbody>
</table>

3.6 Surface and Interfacial Tension Measurement

Surface tension measurements were conducted using the Cenco- Du nöuy Tensiometer, which is capable of measuring both surface and interfacial tension of liquids including those of dispersions. It consists of a platinum-iridium ring suspended from a beam connected to a torsion wire. The liquid is placed in a container which rests on a platform of adjustable height. To measure surface tension, it is recommended that the liquid is to be placed in a container of at least 4.5 cm in diameter. In the present study a glass crucible of 6 cm diameter was used for all surface tension measurements. It can be easily cleaned and the lip allowed easy disposal of test samples.
Experimental procedure used for surface tension measurement was similar to those for most Du nöuy Tensiometers. In contrast to measurement of surface tension of pure liquids, measurement of the interfacial tension of the reactive dispersion using the Du nöuy method would be difficult. The method essentially involves the determination of the forces required to pull the ring through the liquid-liquid interface. The experimental procedure would require the addition of significant quantity of MEA to the measuring container. This would lead to an increase in reaction rate, thus changing the chemistry of the continuous phase. Feasible alternative would be to determine surface tension of each phase and calculate the interfacial tension using empirical correlation. *Antonow’s rule* states that the interfacial tension between two saturated liquid phases ($\sigma_{12}$) equal to the difference between their individual surface tensions with air (Zaldivar *et al*, 1996).

\[ \sigma_{12} = |\gamma_1 - \gamma_2| \] (3.1)

This relationship has been successfully used to determine the interfacial tension for liquid-liquid dispersions (Yamamura and Takahashi, 1999; Alopaeus *et al*, 2002).

The surface tension measurements required larger quantity of samples, approximately 60 ml. Thus an electronic pipettor with 10 ml tip was employed to withdraw the required quantity of sample from the sampling region. Once surface tension value of the dispersion was obtained, *Antonow’s* correlation was used to estimate the interfacial tension between phases. Samples were taken at 5, 15, 30, 60, 120, 180, 300 minutes after the commencement of the run. The number of samples taken was less than other tests (such as drop size measurement) due to the comparatively large sample volume required for tests. Even with the reduction of sample numbers, the volume of vessel contents was reduced by 15 % at the end of run. This is likely to have significant impact on the hydrodynamic of the system and is likely to be source of error in interfacial tension results.
3.7 Density Measurement

Density measurement of pure materials was conducted using a density bottle. The measurement simply consisted of simply placing the liquid in the bottle with a precisely known volume (25,015 cm³) and weighing the contents using a high precision electronic balance. Air tight bottle top ensured that volatile materials were not lost due to evaporation. Precautions were taken to ensure that no air bubbles were entrapped in the bottle. Presence of pockets of air in the bottle would lead to error in the measurement. The density of the dispersion during the reaction was also measured using the density bottle.

3.8 Error Analysis

Details of the experiments conducted in the present study have been discussed in previous sections of this chapter and the results produced by these experiments will be presented in the next chapter. As with most experimental studies, there are errors which are inherent with the results produced. Following section aims to briefly the discuss errors arising from experimental measurements.

3.8.1 Drop Size Measurement

Drop size measurements were conducted by sample withdrawal in conjunction with a microscopic video photography. Despite being one of the simplest techniques of drop size measurement, the photographic technique is one of the most accurate (Godfrey and Slater, 1994). Nevertheless, there a number of possible sources of error inherent with the drop size measurement technique adopted for the present study.

Errors could occur as a result of coalescence during sample withdrawal. In the present investigation, samples of the dispersion were withdrawn using a pipetting technique. As such, the force of the suction could cause drops to collide and coalesce. Similar force is required to dispense the contents in the pipette tip to the watch glass, resulting in further coalescence. Constant rate of suction and dispensing was applied to ensure that the flow within the pipette tip was uniform, thereby minimising coalescence. Coalescence may also
have occurred while images were taken. Tests were conducted to determine the variation in drop sizes during photography. Samples of the dispersion were placed on a watch glass and images were taken at regular time intervals. Results show that $d_{32}$ values vary $\pm 4\%$ after a period of 25 minutes and $\pm 7\%$ after 60 minutes from the initial $d_{32}$ value. Drop size distribution of the sample also shows a slight shift towards larger drop sizes with time, an indication of coalescence. However, the errors are likely to be minimal given that the time required for photography was less than 10 minutes. It should be noted that the effect of reaction during photography was also accounted for in the above mentioned error calculations.

Another source error could arise from the measurement of drops in the photographed images. Drops were sized by placing the cursor opposite ends of photographed drops and calculating the number of pixels between the two cursor points. Although the image analysis software used in this study allowed for automated calculation of drop sizes, the placement of cursor points was done manually. Therefore, there is a certain level of error involved as a consequence of the resolution of the human eye. Pacek et al (1994) suggest that when the operator is sitting in front of the screen, the human eye can reasonably distinguish down to 2 to 3 pixels. This is equivalent to a value of approximately $\pm 2 \mu m$. Drops measured were only those which were reasonably in-focus in an image snapshot. There were drops that appeared in images which were out-of-focus due to fact they were behind or in front of the focus depth of the microscope. Drops which were slightly out-of-focus were used because only a small percentage of drops appeared totally in-focus in each image snapshot. As such there were errors associated with the measurement of drops which were slightly out-of-focus. Drops which were in front of the focus depth appeared larger than their actual sizes and conversely, drops which were behind the focus depth appeared smaller. But given that the probability of being of being in front or behind the focus depth of the microscope is equal, the errors are normally distributed and the mean error is reduced to zero with increasing number of drops.

To minimise the time required for the analysis of one population of drop sizes, it is desirable to measure as few drops as possible. On the other hand, the number must be sufficient to give a representative sample. Based on the compromise between the statistical demand on the accuracy of the drop size distribution and the time required for measurement, at least 300
drops were measured for each sample population. Giles et al (1971) proposed that 300 drops would lead to a maximum error of 3% in the measured Sauter mean drop diameter.

Reproducibility of drop size results was accessed by the repetition of experiments under some experimental conditions. Figure 3.14 shows the evolution of $d_{32}$ at 150 rpm for the Rushton turbine impeller.

![Figure 3.14: Evolution of $d_{32}$ for the Rushton turbine impeller at 150 rpm, $\phi = 0.028$.](image)

Results show that the trends of the evolution of $d_{32}$ for the three runs are very similar. In all three cases, the $d_{32}$ increases initially to reach a maximum and then decreases with time. Contrasting, but self consistent trend can be observed with the three runs conducted at 350 rpm (Appendix A.4). These results indicate that the reproducibility of the drop size measurements is quite good. However, there are some deviations of $d_{32}$ values in comparative sample times between the repeated experimental runs. Average absolute deviation $\left( \frac{1}{n} \sum |x - \bar{x}| \right)$, for each sample time of the three runs reaches up to 15%. In most cases the deviation values are less than 10%. The Average value of the average absolute deviation for all sample times at 150 rpm and 350 rpm were found to be 7.7 % and 9.2%
respectively. This suggests that the experimental technique adopted for the drop size measurement is able to reproduce results reasonably well.

### 3.8.2 Reactant Concentration Measurement

Concentration of the reactant, PIBSA, was measured using transmission FTIR spectroscopy with a fixed pathlength solution cell. There have been a number of studies that have utilised FTIR for quantitative chemical analysis (Chiou et al., 1997; Dimitrakopoulos et al., 1996; Storey et al., 1998; Xu et al., 2000; Scott et al., 2003). Investigators such as Papke et al. (1991) have used FTIR to determine the concentration of a PIBSA derivative emulsifier in multi-component systems. Despite its popularity as a tool for quantitative chemical analysis, FTIR spectroscopy may have inherent errors which are associated with the FTIR instrumentation. It is difficult to assess whether these errors exist with the instrumental setup in the present study. Given that all measurements were conducted using the same procedure and instrumental setup, errors associated with FTIR instrumentation would be the uniform for all measurements.

As discussed in section 3.4, the concentration of PIBSA was determined by analysing the intensity of the anhydride band with a peak at 1788 cm$^{-1}$. The band was chosen because it is the most intensive and is relatively isolated from neighbouring bands. Nevertheless, some interference from neighbouring peaks is likely to occur. Figure 3.11 shows that the closest band to the anhydride band is the ester band with a peak at 1740 cm$^{-1}$. This band represents a constituent of the product in the reaction between MEA and PIBSA. As such, the intensity of the ester band is expected to increase with progression of the reaction which also coincides with the decrease in the intensity of the anhydride band. This suggests that the interference of the anhydride band is likely to increase with conversion. Such interference would produce inaccurate intensities of the anhydride band which in turn would lead to erroneous PIBSA concentrations.

Another source of error could arise from reaction progressing during sample withdrawal and chemical analysis. As discussed in section 3.4, steps were taken to minimise this from occurring by keeping the withdrawn samples at low temperatures. However, it would be impossible to eliminate a certain level of reaction from occurring during chemical analysis.
This would result in the detection of lower PIBSA concentrations than actually present in the reactor. Reproducibility of concentration measurements were assessed by the repetition of some experimental runs (Appendix A.4). The average value of the average absolute deviation for the three experimental runs conducted at 150 rpm was found to be 12.3\%.

### 3.8.3 Measurement of Physical Properties

Viscosity of the dispersion was measured using the Carri-Med CSL rheometer with the parallel plate arrangement. The sensitivity of the instrument is such that it is capable of producing measurements with an accuracy which is far beyond the requirement of this investigation. However, there are several possible sources of error with the rheological measurements. One source of error could arise from the fact that the instrument operates in such a manner that the top plate rotates at significant speeds. In a reactive dispersion such as the present case, one would expect the reaction to progress whilst the test is being conducted. To reduce impact this error, only the initial values of viscosity were used for analysis.

Presence of air bubbles was a possible source of error in the interfacial tension and density measurements. Possibly a much more significant source of error with the tests arise from the fact they require large volumes of samples. Significant reduction in the volume of the contents in the reactor leads to significant hydrodynamic disturbance of the system and errors in measurements. To reduce the effect fewer number (as compared to other measurements) of samples were withdrawn and tested.
CHAPTER 4

DROP SIZE STUDY

This chapter presents results produced by the drop size experiments. Results of the evolution Sauter mean drop diameters and drop size distributions at various impeller speeds, dispersed phase volume fractions and impeller types are presented and discussed in detail. Steady state drop sizes produced at various experimental conditions are also subject to discussion. In addition, correlations to predict steady state Sauter drop diameters obtained from the experiments conducted are presented and their validity discussed.
4.1 Evolution of Drop Size

To examine the evolution of drop sizes, samples of the dispersion were withdrawn and photographed at regular intervals during an experimental run. Series of experimental runs were conducted in which the agitation speed and the dispersed phase volume fraction were varied. Agitation speeds examined were 150, 200, 250, 350, 450 and 600 rpm. Dispersed phase volume fractions examined were 0.028, 0.02 and 0.01 (Table 3.5). Number of samples taken for each experimental run ranged between 6 and 10. The drop size distribution and the Sauter mean drop diameter for each sample was obtained by measuring at least 300 drops.

4.1.1 Transient Sauter Mean Drop Diameter

Figure 4.1 shows evolution of $d_{32}$ for the Rushton turbine impeller operating at various speeds. A dispersed phase volume fraction of 0.028 was used for these experiments. At 150 rpm, the Sauter mean drop diameter, $d_{32}$ rapidly increases from 90 $\mu$m to reach a maximum of 120 $\mu$m after approximately 60 minutes from the commencement of agitation. With further elapse of time, $d_{32}$ decreases gradually to reach a value 90 $\mu$m after 300 minutes. Similar trend can be observed at 200 and 250 rpm. However, at these speeds the initial increases in $d_{32}$ was less pronounced than that found at 150 rpm. Furthermore, the maximum $d_{32}$ value was obtained earlier: approximately 40 and 30 minutes at 200 and 250 rpm respectively. At the higher speeds of 350, 450 and 600 rpm, $d_{32}$ values appear to decrease continuously from the commencement of agitation until the end of the experimental run. It should be noted that at higher speeds experiments were stopped at earlier times than those for the lower speeds. The reason for this is that in a reactive system such as the present investigation, the dispersed phase drops are present in the vessel for only limited period of time. This point will be discussed in detail in subsequent sections.
Experimental investigations on the evolution of mean drop size are scarce in literature. Hong and Lee (1985), Tsouris and Tavlarides (1994) and Baldyga et al (2001) examined the transient drop sizes of kerosene/ethyl acetate-in-water, toluene-in-water and chlorobenzene-in-water systems respectively. In these investigations, at all impeller speeds, the mean drop size was found to decrease fairly rapidly with time at the beginning of agitation. Thereafter the drop size gradually decreases to approach a constant value. This trend is similar to the evolution of $d_{32}$ observed at 350, 450 and 600 rpm in the present investigation.

It is well established that when two immiscible liquids are brought into contact in an agitated vessel, the dispersion is formed as a result of two competing processes: the rate at which the bulk liquid of the dispersed phase breaks up into fine drops and the droplet coalescence rate which gives back the bulk liquid (Hong and Lee, 1983). In a typical dispersion, the breakage rate dominates the coalescence rate during the initial period of agitation process until an equilibrium drop size distribution is established. At equilibrium, breakage and coalescence occur at the same rate and there is no further change in mean drop size or drop size distribution (Pacek et al, 1999). This would be an explanation for the trends on the evolution of drop sizes observed by Hong and Lee (1985), Tsouris and Tavlarides (1994) and Baldyga et al (2001). Hong and Lee (1985) also pointed out that the time required to reach the steady
state or equilibrium, varies with the impeller speed. At higher impeller speeds, \( d_{32} \) decreases quite rapidly and reaches steady state at a shorter time as compared to the a case where the impeller operates at lower speed. This appears to be case in the present investigation, specifically with higher impellers speeds (350, 450 and 600 rpm). At 600 rpm, \( d_{32} \) decreases rapidly in the initial stages, before reaching a relatively constant value after 15 minutes. This occurs after 90 and 60 minutes at 350 and 450 rpm respectively. The evolution of drop size at higher speeds appears to be consistent with previous studies (Hong and Lee, 1985, Tsouris and Tavlarides, 1994 and Baldyga et al, 2001). This is despite the major differences in the systems used in the investigations. The above mentioned investigations involved non-reactive liquid-liquid dispersions as opposed to present case where the system is reactive. In the current study, the flow within the stirred tank can be classified as laminar or just transitional flow regime (Appendix A.5), whereas the previous investigations operated at high Reynolds numbers where turbulent flow prevailed.

It can be also seen from figure 4.1 that the evolution of \( d_{32} \) at lower speeds (150, 200 and 250 rpm) is quite different from those at higher speeds (350, 450 and 600 rpm). At low speeds, \( d_{32} \) increases quite rapidly at the initial stages before reaching a maximum value and then starts decreasing continuously. After a long period of agitation \( d_{32} \) appears to reach a relatively constant value. The presence of a maximum in transient \( d_{32} \) curve is quite unusual and to the author’s best knowledge such a trend has not been reported in the literature. It should be noted that present study is a reactive system, where the physical properties are expected to change as the chemical composition of the system changes with time. Consequently, drop coalescence and breakage processes are more complicated than those found in non-reactive dispersions.

The dispersed phase consists of pure MEA and assuming that the reaction does not take place in the dispersed phase, the chemical composition within the dispersed phase remains constant throughout the dispersion process. Therefore it can be expected that the physical properties of the dispersed phase, namely the dispersed phase viscosity (\( \mu_d \)) and density (\( \rho_d \)), would not change with time. In contrast, the physical properties of the continuous phase (viscosity, \( \mu_c \) and density, \( \rho_c \)) and interfacial tension may change as the reaction progresses with time. Therefore experiments were conducted in the present study to measure these properties during the dispersion process.
The average density $\rho_m$ of the two phase dispersion can be calculated as a weight average of the corresponding values of the dispersed and continuous phases, $\rho_d$ and $\rho_c$ respectively (Bouyatiotis and Thornton, 1967).

$$\rho_m = \rho_d \phi + \rho_c (1 - \phi) \quad (4.1)$$

In cases where density difference is small and/or in dilute dispersions, the continuous phase density can be used as the average approximate density of the dispersion. Figure 4.2 depicts the transient average density of dispersion at selected experimental conditions.

![Figure 4.2: Transient density of the dispersion at selected experimental conditions, $\phi = 0.028$.](image)

Time variant density curves show very small change in $\rho_m$ in the 3 hour period and do not appear to vary a great deal. Therefore it is reasonable to suggest that the effect of density on the evolution of drop sizes is insignificant. Similarly as shown in Figure 4.3, interfacial tension also does not appear to change a great deal with time or experimental conditions.
The viscosity of the liquid dispersion, $\mu_m$, can be described by the following semi-empirical equation proposed by Vermeulen et al (1955):

$$\mu_m = \frac{\mu_c}{1 - \phi} \left(1 + \frac{1.5\mu_c\phi}{\mu_d + \mu_c}\right) \quad (4.2)$$

According to the above equation, at low dispersed phase volume fractions and when viscosity ratio, $\mu_d/\mu_c$ is small, the viscosity of the dispersion would be approximately equal to the viscosity of the continuous phase. In the present investigation, $\mu_c$ is significantly larger than $\mu_d$ (small viscosity ratio) and experiments were carried out in dilute conditions ($\phi \leq 0.028$). Therefore it was decided that it would be reasonable to assume that the viscosity of the dispersions measured is equal to the continuous phase viscosity.

In the absence of any significant changes in liquid properties such as the interfacial tension, densities (of both phases) and dispersed phase viscosity during the period of agitation, the presence of peak in transient $d_{32}$ values could probably be explained only on the basis of
changes in the continuous phase viscosity with time. Figure 4.4 shows the change in dispersion viscosity as a function of time.

![Graph showing viscosity changes with time and impeller speed]

Figure 4.4: Transient viscosity of the dispersion with the Rushton turbine impeller at various speeds, $\phi = 0.028$.

As the reaction progresses, it can be seen that the dispersion (or continuous phase) viscosity increases with time due to the formation of products and their dissolution in the continuous phase. Eventually the $\mu_c$ reaches a constant value indicating the near completion of the reaction. The rate at which the $\mu_c$ approaches the final value however, varies with the impeller speed. At low impeller speeds, the constant value is reached in a longer period of time compared to higher speeds. In fact at 150 rpm, it appears that the $\mu_c$ continuously increases until the end of the experimental run.

Stamatoudis and Tavlarides (1985) were one of a few investigators to examine the effect of continuous phase viscosity on the drop sizes in liquid-liquid dispersions. They studied the steady state Sauter mean drop sizes in kerosene-aqueous glycerol ($3.6 \text{ cP} < \mu_c < 223.1 \text{ cP}$) and mineral oil-aqueous glycerol ($3.5\text{cP} < \mu_c < 122.6 \text{ cP}$) for impeller Reynolds numbers ranging from 358 to 23467. Their findings provide a possible explanation for the evolution of $d_{32}$ values observed in the present investigation. Stamatoudis and Tavlarides (1985)
reported that at low impeller speeds, the Sauter mean drop diameter increases initially with the continuous phase viscosity, reaches a maximum then decreases. It is clear that their results have some parity with trends observed at 150 rpm in the present investigation. In terms of the effects of $\mu_c$ on the breakage and coalescence processes, Stamatoudis and Tavlarides (1985) suggested that breakage rate decreases with increasing $\mu_c$, resulting in the initial increase of $d_{32}$. A still further increase of $\mu_c$ causes the coalescence rate to decrease, resulting in the decrease of $d_{32}$ after reaching a maximum. Any further increase in $\mu_c$ results in a region in which $d_{32}$ remains constant. This result occurs probably because the decrease in breakage rate is counter balanced by the decrease in the coalescence rate.

Stamatoudis and Tavlarides (1985) also found that at higher impeller speeds, $d_{32}$ decreases slightly with $\mu_c$, reaching a minimum and then increases to an almost constant value. The initial decrease in $d_{32}$ in contrast to the increase that occurs at lower speeds was attributed to the influence of the coalescence rate because of the relatively smaller drop size present at these speeds. Thus at higher speeds the coalescence rate decreases as $\mu_c$ increases, resulting in the initial decrease in $d_{32}$. As $\mu_c$ increases further, the breakage rate decrease further to overcome the decrease in coalescence rate. As a result, $d_{32}$ reaches minimum and starts increasing. The relatively constant value of $d_{32}$ which results thereafter is due to the attainment of equilibrium between the coalescence and breakage processes. However, such a trend was not observed in the present investigation. At higher impeller speeds (350, 450 and 600 rpm), $d_{32}$ decreases continuously with time before reaching a relatively constant value. These trends resemble those observed in previous studies where continuous phase viscosity was held constant (Hong and Lee, 1985, Tsouris and Tavlarides, 1994 and Baldyga et al, 2001). A reason for the disparity with the finding of Stamatoudis and Tavlarides (1985) at high speeds could be due the possibility that impeller speeds used in the present investigation did not reach the levels which Stamatoudis and Tavlarides (1985) considered high. Impeller speeds used in the present investigation may have been equivalent to the low to moderate speeds used by Stamatoudis and Tavlarides (1985). If this was the case, the differing trends observed at high (350, 450 and 600 rpm) and low (150, 200 and 250 rpm) impeller speed can probably be explained from the change in $\mu_c$ with time. It can be seen from Figure 4.4, that the viscosity reaches a constant value earlier at higher impeller speeds. Thus the period of time during which $\mu_c$ affects the breakage and coalescence processes becomes shorter progressively with increasing impeller speed. At the highest impeller speed, 600 rpm, $\mu_c$
becomes constant almost immediately after the commencement of agitation. As a consequence, $\mu_c$ affects the breakage and coalescence processes only during the initial period of agitation and therefore its impact would not be significant on the overall trend of $d_{32}$ values. Such rationale also provides an explanation for the existence of the prominent peak observed in the evolution of $d_{32}$ at 150 rpm and those of less prominence at 200 and 250 rpm.

The $d_{32}$ results that have been discussed thus far are for the dispersed phase volume fraction, $\phi = 0.028$. Similar experiments were conducted for lower dispersed phase volume fractions of $\phi = 0.02$ and $\phi = 0.01$ and the $d_{32}$ results obtained for these are shown in Figure 4.5 and Figure 4.6.

Figure 4.5: Evolution of $d_{32}$ for the Rushton turbine impeller at various speeds, $\phi = 0.02$. 
For $\phi = 0.02$, the evolution $d_{32}$ at 250,350 and 450 rpm is similar to those found at lower speeds (150, 200 and 250 rpm) for $\phi = 0.028$. The $d_{32}$ value increases initially to reach a maximum and decreases gradually thereafter. In terms of the dynamics of the breakage and coalescence processes, it appears that the initial rise in $d_{32}$ is due to the dominance of drop coalescence rate over the breakage rate. With increase in time, the dominance of the coalescence rate would gradually diminish to a point where the breakage rate begins to dominate the dispersion process. This competition between the coalescence and breakage processes probably lead to the maximum in $d_{32}$ and the following decrease. In the previous sections in this chapter it was argued that changes in the relative rates of breakage and coalescence process is due to the variations in continuous phase viscosity with time. Time variant viscosities of the dispersion at various speeds for $\phi = 0.02$ is shown in Figure 4.7.
Figure 4.7: Transient viscosity of the dispersion with the Rushton turbine impeller at various speeds, $\phi = 0.02$.

Figure 4.7 shows an increase in viscosity with time for all impeller speeds. The magnitude of increase in viscosity appears to progressively increase with increasing agitation speed which is also the case for $\phi = 0.028$. However, the viscosity stabilises at a lower value of approximately 5-6 Pa.s. This value is found to be approximately 9-10 Pa.s for $\phi = 0.028$. Given the similar transient trends of viscosity for both dispersed phase volume fractions, the arguments that are used to explain $d_{32}$ results based on the relative rates of coalescence and breakage processes for $\phi = 0.028$ can also be used to explain the evolution trends of $d_{32}$ for $\phi = 0.02$.

It is evident from transient $d_{32}$ curves shown in Figure 4.5 that the evolution of $d_{32}$ at 150 rpm is quite different from those observed at higher speeds (250, 350, and 450 rpm). The $d_{32}$ continues to increase with time to reach a relatively constant value after long period of agitation. The $d_{32}$ does not decline at any stage. A peak that was present for higher speeds is absent at 150 rpm. This trend could be attributed to the change in $\mu_c$ with time at the speed (Figure 4.7): At 150 rpm, $\mu_c$ increases at a slower rate than that for higher speeds. For instance, $\mu_c$ of 4 Pa.s is reached after approximately 120 minutes at 150 rpm as compared to 20 minutes at 350 rpm. On examining the trends of $d_{32}$ and viscosity values at all speeds, it is
apparent that below the viscosity of 4 Pa.s, $d_{32}$ increases with time. It indicates that for $\mu_c < 4$ Pa.s, the coalescence rate is comparatively higher than the breakage rate. To further reinforce this observation, one must examine the evolution of $d_{32}$ for $\phi = 0.01$ (Figure 4.6). The $d_{32}$ increases initially before reaching a relatively constant value with further elapse of time. The trend is slightly different at 150 rpm where $d_{32}$ increases continuously with time. This suggests that coalescence rate dominates the breakage rate during the dispersion process throughout the experimental run. Based on the arguments used earlier one would expect $\mu_c$ to be relatively low ($\mu_c < 4$ Pa.s). It is confirmed in Figure 4.8 which shows that the viscosity does not exceed 4 Pa.s throughout the experimental run.

![Figure 4.8: Transient viscosity of the dispersion with the Rushton turbine impeller at various speeds, $\phi = 0.01$.](image)

Examining all $d_{32}$ curves for various speeds and dispersed phase volume fractions, it is apparent that four different trends are present. It is also apparent that agitation speed and dispersed phase volume fraction determine the likely trend. The observed trends are:
Trend 1: Sauter mean drop diameter, $d_{32}$ decreases initially and reaches a constant with time. This trend is observed mainly at high dispersed phase volume fractions and high impeller speeds.

Trend 2: $d_{32}$ increases initially, reaches a maximum value and decreases with time (possibly will reach a constant value after a long period of time). This is likely to occur at high dispersed phase volume fractions and low impeller speeds or moderate dispersed phase volume fractions and high impeller speeds.

Trend 3: $d_{32}$ increases initially and attains a constant value after long period of agitation. It occurs at moderate dispersed phase volume fraction and low impeller speeds or low dispersed phase volume fraction and moderate to high impeller speeds.

Trend 4: $d_{32}$ increases continuously with time. It is likely to occur at low dispersed phase volume fractions and low impeller speeds speed.

4.1.2 Evolution of Drop Size Distribution

In the previous section, the evolution of $d_{32}$ at various impeller speeds and dispersed phase volume fractions was discussed. The changes in $d_{32}$ values alone do not divulge the dispersion process completely. As suggested by Zhou and Kresta (1998b), it is possible to obtain similar $d_{32}$ values for different types of drop size distributions. Thus, to describe a dispersion, both the mean drop size and the drop size distribution (DSD) are needed. In the present investigation DSD was determined by measuring at least 300 droplets for each sample and classifying them in $10 \, \mu m$ size intervals. Trendlines that encompasses the distribution is presented in respective figures along with each DSD data set. Agreement between the data set and the trendlines were assessed using Coefficient of determination, $R^2$ (see Appendix A.4 for $R^2$ values). As discussed earlier, samples were taken at regular intervals during each experimental run. The number of samples taken for each experimental run varied depending on the impeller speed and the dispersed phase volume fraction. The transient $d_{32}$ curves indicated that there are four distinctive trends amongst all the results. DSD related to each of these cases will be discussed below:
Results presented in Figure 4.9 clearly show that the distribution curves narrows and shifts towards smaller drop size with increase in time. These results are consistent with the results reported in literature for liquid-liquid dispersions. Sathyagal and Ramkrishna (1996) obtained DSD data for four different liquid-liquid systems and their results exhibited trends similar to those in Figure 4.9. Similar results were also reported by Tsouris and Tavlarides (1994) for a toluene-water system and Yang et al (2000) for styrene-aqueous poly (vinyl alcohol) system. These authors’ results also showed that the change in distribution is quite rapid initially, but the rate of change diminishes with time. After a long period of stirring time, 50 minutes in the case for Yang et al (2000), the distribution however remained more or less the same. The authors suggested that at this point a dynamic equilibrium between the coalescence and breakup processes is established. Figure 4.9 also indicates a rapid narrowing of DSD and shift towards smaller drop sizes in the initial stages of agitation. Sathyagal and Ramkrishna (1996) suggested that in the initial stages of a breakage experiment, the drop size-size distribution changes rapidly due the presence of larger droplets which breakup more readily. With the production of smaller droplets, these breakage events would become less frequent. Eventually, the equilibrium is attained and distribution becomes constant. In the
present case, the DSD at 60 and 90 minutes are relatively the same indicating the attainment of equilibrium between the breakage and coalescence processes.

Evolution of DSD at various impeller speeds and dispersed phase volume fractions were investigated by Sathyagal and Ramkrishna (1996) and Tsouris and Tavlarides (1994), respectively. Their results showed that the DSD narrowed and shifted towards smaller drop sizes with time for all impeller speeds and dispersed phase volume fractions. In the present investigation, the evolution of DSD varied markedly for some impeller speeds and dispersed phase volume fractions.

Results presented in Figure 4.10 shows the evolution of DSD for an impeller speed of 150 rpm. These results clearly show that the evolutionary path of DSD at 150 rpm is sufficiently different from that observed for 450 rpm (Figure 4.9). Initially the distribution curve broadens quite rapidly and shifts towards larger drop sizes indicating coalescence between droplets is dominating. This is followed by a narrowing of the distribution curve and a shift towards smaller drop sizes. With further increase in time, the narrowing of the DSD curve appears to diminish before becoming relatively constant suggesting the attainment of steady
state. These findings are different from the findings from the researchers such as Sathyagal and Ramkirshna (1996).

Hong and Lee (1983) also found that a narrowing of DSD with time, but their results varied slightly with energy input or associated impeller speed. They observed that at low levels of energy input, the distribution approaches a normal distribution as steady state is achieved. On the other hand, at higher energy input levels, the distribution moves towards a skewed or log-normal distribution. In the present investigation, the distribution at relatively higher speeds (i.e. 450 rpm) appears to become normal distribution with time, whereas at 150 rpm the distributions are entirely log-normal.

With the lower dispersed phase volume fraction, $\phi = 0.01$, the evolution of DSD at 350 and 150 rpm are presented in Figures 4.11 and 4.12 respectively. These results are significantly different from those for $\phi = 0.028$. Figure 4.11 shows that the DSD curve broadens and shifts toward larger drop sizes with increase in time. Initially the change in DSD appears to be fairly rapid, but the rate of change decrease with time. Similar to the results for 350 rpm, the evolution of DSD at 150 rpm shows the distribution broadening and shifting towards larger drop sizes as time progresses. However, the rate of change of DSD appears to be fairly constant throughout the dispersion process and does not decrease with time. In both cases, the distribution was log-normal at all times. All distributions have a peak at the low diameter side and a long tail on the large diameter size.
Figure 4.11: Evolution of DSD for the Rushton turbine impeller at 350 rpm, $\phi = 0.01$.

Figure 4.12: Evolution of DSD for the Rushton turbine impeller at 150 rpm, $\phi = 0.01$. 
The four cases examined show four distinctive trends of DSD just as their $d_{32}$ results. In fact, the trends in $d_{32}$ values provide an insight into DSD results and vice versa. For conditions where $d_{32}$ decreases with time, the DSD narrows and shifts towards smaller drop sizes. When $d_{32}$ increases, the DSD broadens and shifts towards larger drop sizes. The transient $d_{32}$ curves indicate that there are four distinctive trends that are present among all the results and similarly, four different trends of the evolution of DSD were found for all DSD results (see Appendix A.6 for remaining DSD results).

It was established earlier that the change in viscosity has a significant impact on the evolution of $d_{32}$ and DSD. Given the relationship between product formation and dispersion viscosity, the reaction can be considered to have an indirect effect on drop sizes. Nagata (1975) suggested that drop sizes decrease as a direct result of reaction. They assumed that the outer layer of the dispersed drop gets consumed by the reaction and slowly diminishes in size with time. This is contrary to the finding by Hiraoka et al (1990). They investigated the change in drop sizes in a system where n-amyl acetate was dispersed and reacted with sodium hydroxide and found that the $d_{32}$ was almost constant during the reaction period although the number of droplets decreased with time. Similarly in the present investigation, droplets did not decrease in size a direct result of the reaction. In some instances drops actually increased in size due to coalescence. Furthermore video images showed that the population density of droplets continually decrease with the progression of the reaction. Figure 4.13 shows drop images obtained for an impeller speed of 350 rpm and $\phi = 0.028$. It can be seen that a large number of droplets present after 15 minutes of the experiment and fewer droplets at 30 minutes. This trend continues with time until there is no droplet present after about 4 hours (240 minutes).
Figure 4.13: Video images taken at various times for the Rushton turbine impeller operating at 350 rpm and $\phi = 0.028$. 
4.2 Steady State Drop Size

In the previous section, the discussions were mainly on the evolution of Sauter mean drop sizes. Results have shown that there are several evolutionary trends. Relating the varying values of $d_{32}$ to experimental conditions will be a difficult task. The process would be simplified if a single value of $d_{32}$ is used to develop functionality with parameters including physical properties, vessel geometry and operating conditions. It can be clearly seen that if the dispersion is maintained by agitation for a sufficiently long period of time, a dynamic equilibrium between coalescence and breakage processes will be established. Under such condition, a steady state or equilibrium Sauter mean drop diameter can be observed (Liu and Li, 1999). The time required for the drops to reach the steady state size varies widely for different liquid-liquid systems. In addition, the equilibrium time depends both on operating variables such as agitation speed and the dispersed phase volume fraction (Ruiz et al., 2002). However, Arai (1977) found that a higher rate of rotation of the agitator had only a small effect on the time required to reach equilibrium state.

Physical properties of both the continuous and dispersed phases also have an impact on the time required to reach the equilibrium drop size. Under certain conditions, the time required to reach the steady state can be only few minutes (Hong and Lee, 1985) while in other case it can be more than several hours (Apostoliduo and Stamatoudis, 1991). Majority of drop size studies that have been reported in the literature are for non reactive dispersions. In such systems, sufficient time can be allowed for the dispersion to reach steady state drop size. In contrast, the present system is reactive. The dispersed MEA droplets react with PIBSA in the continuous phase and completely disappear after a certain period of time. As such drops may not remain in the system long enough to reach the equilibrium size and it is difficult to conclude whether the equilibrium drop size is reached or not.

Even in well established fully turbulent (and non-reactive) dispersions, the determination of steady state drop size is not a straightforward task that leads to a definitive answer. There is evidence to suggest that the maximum stable drop size ($d_{\text{max}}$) decrease even after a long mixing time period and that it reaches values significantly smaller than what was earlier considered a fair estimate of $d_{\text{max}}$ (Lam et al, 1996). For this reason, complete reliance on critical droplet size in apparatus design may not be warranted (Kostoglou and Karabelas,
Nevertheless, estimate of \( d_{\text{max}} \) has been of practical interest in design and cannot be rendered useless. In the present investigation, the final drop size obtained for given experimental condition is assumed to be the equilibrium size. For instance, Rushton turbine operating at 350 rpm and dispersed phase volume fraction \( \phi = 0.028 \), the final Sauter mean drop size is 33 \( \mu \text{m} \). This value will be used as the steady state drop size for discussions in the following sections.

### 4.2.1 Steady State Sauter Mean Drop Diameter

A plot of steady state Sauter mean drop diameter, \( d_{32}^* \) versus impeller speed, \( N \) at various dispersed phase volume fractions is shown in Figure 4.14. In these cases, 6-bladed Rushton turbine impeller was used to provide the agitation.

It is evident that the mean drop size progressively becomes smaller with increasing impeller speed. This trend was observed by most investigations in various liquid-liquid systems (Sprow, 1967; Gallego-Lizon and Perez de Ortiz, 2000; Ban et al, 2002; Brown and Pitt, 1970; Maggioris et al, 2000). However, trends that are different from the above have also been observed in some liquid-liquid dispersions. A U-shaped dependence of mean drop size
on agitation speed has been reported by several investigators (Tanaka and Hosogai, 1990; Chatzi and Kiparissides, 1995; Zhou and Kresta, 1998b). As the agitation rate increases, the droplet size decreases, reaches a minimum value, and then starts increasing with speed. The reason ascribed to this trend is that as the interfacial area increases due to the reduction in droplet sizes, the effectiveness of the surfactant molecules on the interface diminishes. This probably results in coalescence and therefore, to a size increase of the droplets (Pacek et al., 1999). The present system did not contain a surfactant and the result showed that interfacial tension remained relatively constant throughout experimental runs (Figure 4.3). Thus the U-shaped behaviour was not expected nor observed in the present system.

Most of the investigations that examined the relationship between steady state d_{32} and impeller speed, N have found an inverse relationship between the two parameters. This relationship was found to be true irrespective of the dispersed phase volume fraction (Mlynek and Resnick, 1972; Coulaloglou and Tavlarides, 1976; Kraume et al., 2004), tank diameter (Okufi et al., 1990), dispersed phase viscosity (Wang and Calabrese, 1986) and dispersion viscosity (Ohtake et al., 1987). These investigations were however carried out at high Reynolds numbers (N_{Re} > 10,000) where turbulent flow prevails. There have been some investigations that produced comparable results in systems at low Reynolds numbers ranging from laminar to low-transitional. Studies on dispersions of Aqueous sodium caseinate-aqueous sodium alginate (Pacek et al., 2001), several non-Newtonian systems (Shimizu et al., 1999) and kerosene and mineral oil dispersed in aqueous glycerol (Stamatoudis and Tavlarides, 1985) found to produce smaller droplets with increasing agitation rates. The decreasing tendency of the droplet sizes with increasing impeller speed can be explained in terms of higher breakage frequency (Chatzi and Kiparissides, 1995). For breakage to occur, it is necessary that enough energy be supplied to the drop to overcome the force that holds it together due to the surface tension. The energy for the breakage will come from the field outside the drop either as kinetic energy in the turbulent eddies or as shear energy or as a combination of the two. An increase in impeller speed induces greater kinetic energy or/and shear energy on the hydrodynamic field outside the drops.

In dilute dispersions, when a turbulent flow regime is well established the drop size depends on We^{-0.6}. Given that We = \rho N^2 D^3/\sigma, the relationship between the Sauter mean drop diameter and the impeller speed can be expressed as d_{32} \propto N^{-1.2}. This dependence was observed in a diverse range of liquid-liquid systems and conditions such as suspension

Based on the experimental results and theory, most drop size correlations are expressed in terms of Weber number to the power -0.6, thus requiring the exponent of N to be -1.2. However, there have been several investigations which produced different dependencies of \( d_{32} \) on the impeller speed. Values of the exponent for N varying from -0.63 to -1.25 have been reported in the literature (Okufi et al, 1990). Gallego-Lizon and Perez de Ortiz (2000) obtained an exponent -1.12 in their investigation of a water-in-oil emulsion. Others have produced even smaller value of the exponent, such as -0.96 (Bouyatiotis and Thornton, 1967), -0.72 (Roger et al, 1956), and -0.63 (Weinstein and Treybal, 1973). Shinnar (1961) produced an exponent of -0.75, which has been deduced for systems dominated by coalescence. On the other hand, experimental results for a dilute system from Baldyga and Bourne (1993) led to an exponent of -1.8.

The dependency of \( d_{32} \) on N can best be represented by a log-log plot of the two parameters. Figure 4.15 shows such results for the present investigation.
The slopes of the plot were determined using the method of least squares. The $R^2$ (coefficient of determination or correlation coefficient) value for the curves was 0.98 and above, which is an indication of good agreement between the curves and the data sets. These results show that the exponent varies with the dispersed phase volume fraction. The exponents were -1.07, -1.31 and -1.19 for $\phi = 0.028$, 0.02 and 0.01 respectively. Clearly exponents were not equal to -1.2 as prescribed by classical drop breakage theory of Kolmogoroff (1949) and Hinze (1955). Nevertheless, the linear relationship $d_{32}^*$ versus $N$ on log-log plot is consistent with the observations made by previous researchers and the values of the exponents are within the general range of results reported in those investigations. However, the trend in exponent values with respect to dispersed phase volume fraction differs from the reported cases. In general, dilute dispersions are expected to produce larger values of the exponent as compared to those with a higher dispersed phase volume fractions. The reason for this is that an increase of dispersed phase volume fractions results in greater number of droplets per unit volume and therefore a greater coalescence rate. In the present case, moderate dispersed phase volume fraction ($\phi = 0.02$) produces a lower value of the exponent as compared to low ($\phi = 0.01$) and high ($\phi = 0.028$) dispersed phase volume fraction. These results suggest that the exponent decreases in value with the dispersed phase volume fraction.
volume fraction reaching a minimum before increasing further. Possible reason for this trend can be attributed to the variation in continuous phase viscosity that is associated with the respective dispersed phase volume fractions. Figure 4.4, 4.7, and 4.8 show the time variant viscosity of the dispersions at these three dispersed phase volume fractions. The steady state viscosity are 9 to 10, 5 to 6 and 2 to 4 Pa.s for $\phi = 0.028$, 0.02 and 0.01 respectively. These results suggest that the dispersion viscosity increases with increasing dispersed phase volume fraction. Results reported by Stamatoudis and Tavlarides (1985) suggest that the variation in continuous phase viscosity, $\mu_C$ has an effect on the relationship between $d_{32}$ and $N$. They found that the exponent initially decreases with increasing $\mu_C$, reaches a minimum and continuously increases thereafter. Their findings certainly agree well with those observed in the present investigation and indicate that the continuous phase viscosity has a greater influence on the relationship between $d_{32}$ and $N$ than the dispersed phase volume fraction.

### 4.2.1.1 Steady State $d_{32}$ versus $\phi$

The influence of $\phi$ on steady state $d_{32}$ at various speeds is shown in Figure 4.16.

![Figure 4.16: Steady state Sauter mean drop diameter, $d_{32}^*$ versus dispersed phase volume fractions, $\phi$ at various impeller speeds for the Rushton turbine impeller.](image-url)
The slopes of the plots were determined using the method of least squares. The $R^2$ values are greater than 0.97 indicating fairly good agreement between the curve and $d_{32}$ data. These results clearly show that increasing $\phi$ causes the $d_{32}^*$ to decrease for the four speeds used. This trend is totally opposite of what has been reported in previous drop size investigations. Most of the studies found that $d_{32}$ increase linearly with increasing dispersed phase volume fraction.

Drop size correlations of liquid-liquid dispersion in turbulent stirred vessel suggest a linear dependence of $d_{32}$ on $\phi$, which has been expressed as (Coulaloglou and Tavlarides 1976):

$$\frac{d_{\text{max}}}{D} = C_4 (1 + C_5 \phi) We^{-0.6} \tag{4.3}$$

This relationship is supported by experimental observations in various investigations. Kuriyama et al (1996) found that steady state $d_{32}$ steadily increases with an increase in $\phi$. The linear relationship between $\phi$ and $d_{32}$ was observed in a number of systems with varying dispersed phase viscosities ($1.054 \text{ Pa.s} < \mu_d > 0.0107 \text{ Pa.s}$). Several other researchers also found the linear dependency to exist in their agitated systems (Brown and Pitt, 1970; Colulaloglou and Tavalarides, 1976; Mlynek and Resnick, 1972; Okufi et al, 1990). In the cases of Brown and Pitt (1970) and Mlynek and Resnick (1972), linear dependency of $d_{32}$ on $\phi$ was not found at $\phi > 0.3$ and $\phi > 0.2$, respectively (Calabrese et al, 1986b). The trend of $d_{32}$ increasing in a linear manner with $\phi$ was also found in a mixer-settler extraction column for three different liquid-liquid extractions systems (Ban et al, 2002).

There have been several investigators who found that the linear relationship between $d_{32}$ and $\phi$ does not hold. Kraume et al (2004) observed an increase in the $\phi$ resulted in larger drops and a decrease in the slope of $\phi$-$d_{32}$ curves. With increasing $\phi$, the influence on $d_{32}$ appeared to decrease. Similar trend was observed by Godfrey et al (1989) when a pump mix impeller was used. The relationship was nonlinear over a wide range of dispersed phase volume fractions, but appeared to be almost linear for a low $\phi$ values ($\phi < 0.25$). A weak effect of the $\phi$ on $d_{32}$ was observed at all conditions investigated by Gallego-Lizon and Perez de Ortiz (2000). In general $d_{32}$ is found to be directly proportional to $\phi$ in all these cases regardless of
agitation speed, liquid properties or tank geometry. It is well established that $d_{32}$ depends on the dynamics of the breakage and coalescence processes and the influence of $\phi$ on these processes gives rise to relationship between $d_{32}$ and $\phi$.

The presence of a greater amount of dispersed phase affects the equilibrium drop size in two ways. When drops are in close proximity, the small-scale structure of the continuous phase is altered, thereby decreasing the turbulent energy acting to disrupt the drop (Calabrese et al., 1986b). Furthermore, higher dispersed phase volume fractions also leads to a growing collision rate of drops resulting in an increasing number of breakage and coalescence processes. Given that the coalescence process requires the collision between drops and the number of collisions between drops is greater with increased dispersed phase fraction, the increase in coalescence rate is more pronounced than the breakage rate. Both effects lead to an increase in $d_{32}$. Doulah (1975) and Brown and Pitt (1972) however believed that, given that the drop sizes in the vicinity of the impeller has been shown to be determined by break-up mechanism, the effect of $\phi$ on $d_{32}$ is due to the damping effect of the dispersion on turbulence and not due to coalescence.

In contrast to theoretical rationale, experimental results found in the present investigation show an inverse relationship between $\phi$ and $d_{32}$. This could be attributed to the variable steady state $\mu_C$ that is associated with $\phi$ (Figure 4.4, 4.7, and 4.8). Results show that $\mu_C$ increases with $\phi$. As discussed in earlier, the value of viscosity in a dispersion is determined by the conversion of the reactants and the level of product concentration in the system. There have been several investigations in the past that studied the effect of $\mu_C$ on drop sizes.

Dokic-Baucal et al (2004) prepared several emulsions using a homogeniser and studied the drop size as a function of $\mu_C$. Results indicated that systems with higher $\mu_C$ consistently produced smaller droplets compared to low viscosity emulsions. Ludwig et al (1997) produced data which illustrated the effect of $\mu_C$ on the drop sizes in a continuous screw loop reactor. They found that drop sizes increase minutely with increasing viscosity before decreasing significantly with further increase of $\mu_C$. Results produced by Dokic-Baukal et al (2004) and Ludwig et al (1997) suggest that drop size have a tendency to decrease with increasing $\mu_C$. When the viscosity of the continuous phase is increased, the interfacial area increases ($d_{32}$ decreases), which can be explained on the basis of hindrance of coalescence.
Given that $\mu_C$ is indirectly proportional to the dispersed phase volume fraction, the trend depicted in Figure 4.16 seems quite feasible. Stamatoudis and Tavlarides (1985) reported results that are in some instances contradictory to this assertion. They showed that at lower impeller speeds $d_{32}$ increased initially with increasing $\mu_C$ before decreasing. Opposite trend was observed at higher impeller speeds, but the magnitude of change in $d_{32}$ was significantly lower than that at lower speeds. In both cases, $d_{32}$ is relatively constant at the high $\mu_C$ values.

Drop size results produced by Godfrey et al (1989) found that there isn’t a significant difference in slopes of $d_{32}$ vs $\phi$ curves with respect to impeller speeds. Most investigations that examined the effect of $\phi$ on $d_{32}$ did not present the data in a manner such that the effect of impeller speed on the relationship can be determined. Figure 4.16 shows the $d_{32}$-$\phi$ curve progressively decreasing with increasing impeller speed. This trend suggests that the effect of $\mu_C$ on $d_{32}$ is less significant at higher speeds. The dispersed phase volume fraction may have had some direct influence on the dispersion process via increased coalescence rate. However the converse trend of $d_{32}$ vs $\phi$ suggests that impact of $\phi$ is insignificant compared to that of $\mu_C$.

### 4.2.2 Steady State Drop Size Distribution

The influence of impeller speed on steady state drop size distribution at dispersed phase volume fractions of 0.028 and 0.01 are shown in Figures 4.17 and 4.18 respectively. Similar plot for DSD at $\phi = 0.02$ can be found in Appendix A.7.
Figure 4.17: Steady state DSD for the Rushton turbine impeller at various speeds, $\phi = 0.028$.

Figure 4.18: Steady state DSD for the Rushton turbine impeller at various speeds, $\phi = 0.01$. 
It can be seen that in both cases an increase in impeller speed produces narrower distribution with a shift towards smaller drop size. The increase in agitation speed usually results in the decrease of number of larger drop whilst the number of smaller drops increases. This trend was observed in virtually all the studies that examined the effect of impeller speed on DSD. For example, narrowing of DSD with increase in impeller speed was in toluene-water dispersion (Schulze et al, 2000), liquid-liquid emulsion containing a surfactant (Gallego-Lizon and Perez de Ortiz, 2000), a number of dispersions of varying dispersed phase viscosities and interfacial tension (Wang and Calabrese, 1986) and continuous liquid-liquid mixers (Godfrey et al, 1989). Several systems operating at low Reynolds numbers (laminar to low transitional) also exhibited the similar behaviour (Shimizu et al, 1999). This clearly suggests that the drop breakage rate increases with impeller speed.

Many studies on liquid-liquid agitated systems found that DSD exhibits normal distribution at various impeller speeds (Gallego-Lizon and Perez de Ortiz, 2000; Okufi et al, 1990; Schulze et al, 2000). Nagata (1975) suggested that distribution of drop shift from normal to log-normal as stirrer speed increases with the trend being more pronounced for systems with low interfacial tension. However, the trend observed in the present investigation is opposite of what has been generally reported in the literature. The DSD appears to shift from log-normal to normal with increase in impeller speed. However, in majority of these cases, the distribution is skewed towards larger drop sizes. Log-normal distributions are usually found in concentrated dispersions or when chemical reaction or mass transfer occur (Godfrey and Grlic, 1977). This notion is certainly valid in the present investigation as mass transfer and chemical reaction both occur simultaneously.

Figures 4.19-4.20 depicts the effect of dispersed phase volume fraction on DSD at 450 and 150 rpm respectively. Plots for the remaining impeller speeds can found in Appendix A.7.
Figure 4.19: Steady state DSD for the Rushton turbine impeller at various dispersed phase volume fractions, $N = 450$ rpm.

Figure 4.20: Steady state DSD for the Rushton turbine impeller at various dispersed phase volume fractions, $N = 150$ rpm.
It can be seen that DSD narrows and shifts towards smaller drop sizes with increasing $\phi$. Increase in peak height of the DSD curve and a decrease of the fraction of larger drops with the increase in $\phi$ are clearly seen for 450 rpm. This is the general trend observed for all speeds, but it is in total contrast to those observed in previous investigations. Okufi et al (1990) reported that drop sizes distribution becomes wider and the mean drop size shifts to larger values as $\phi$ increases at all stirred speeds investigated. Kraume et al (2004) found that DSD exhibits normal distribution for all dispersed phase volume fractions (0.05 to 0.5) used. Their results also showed that there is only a slight increase in the broadness of the distribution with increasing dispersed phase volume fraction. The distribution was found to merely shift towards larger drop sizes as the dispersed phase volume fraction increases. Brown and Pitt (1972) measured the equilibrium drop size distribution in low-viscosity dispersed phases for a range of $\phi$ ($0.05 \leq \phi \leq 0.2$). They found that drop size volume distributions are approximated by normal distribution even though they tend towards bimodal form as $\phi$ increases. The trend of broadening DSD curves and shift towards larger drops is generally attributed to increase in collision rate of drops and the damping of turbulence which collectively lead to an increase in the coalescence rate and a reduction in the breakage rates.

The trends observed in the present investigation could be resulting from the variation of continuous phase viscosity, $\mu_C$. It has been shown earlier that the steady state $\mu_C$ increases with dispersed phase volume fraction. There has been some evidence to suggest that $\mu_C$ has an impact on the DSD (Noro, 1978; Stamatoudis and Tavlarides, 1985). Stamatoudis and Tavlarides (1985) found that a decrease in $\mu_C$ results in the broadening of DSD and a shift towards larger sizes. The effect was found to be more significant when viscosity ratio, $\mu_d/\mu_C$ is large. Noro (1978) found that as the viscosity ratio ($\mu_d/\mu_C$) decreases, the drop size distribution broadens. Their results indicated that the DSD exhibits log-normal distribution at lower viscosity ratios. These results are comparable with results obtained in the present investigation where the DSD broadens with decreasing dispersed phase volume fraction which is associated with a decrease in $\mu_C$ or an increase in viscosity ratio.
4.3 Impeller Comparison

4.3.1 Evolution of Sauter Mean Drop Diameter

In the past, most of the work has been carried out by studying the drops formed by a flat vertical six-blade disk style impeller or more commonly referred to as the six-bladed Rushton turbine impeller. Examples of investigations that employed the use of Rushton turbine impellers include Roger et al (1956), Mlynek and Resnick (1972), Eckert et al (1985), Calabrese et al (1986), Legisetty et al (1986), Okufi et al (1990), Kuriyama et al (1996), Gallego-Lizon et al (2000) and Kraume et al (2004). In comparison, the use of other types of impellers is quite minimal. Four-bladed paddles (Vermeulen et al, 1955; Calderbank (1958), and propeller (Pavlushenko and Yanishevskii, 1959) were also used to provide agitation in liquid-liquid systems. Several investigators have also compared the effect of various types of agitators on $d_{32}$ and DSD (Kafarov and Babanov, 1959; Rodriguez et al, 1961; Fernandes and Sharma, 1967; Pacek et al, 1999; Sechremeli et al, 2006). Present study employs two different types of impellers, namely 6-bladed Rushton turbine and 3-bladed marine propeller. Both impellers are of equal diameter.

All the results presented so far in this chapter were obtained using the Rushton turbine impeller. Effects of impeller speed and dispersed phase volume fraction on $d_{32}$ and drop size distribution were examined. Similar experiments were conducted using the marine propeller. The impeller speeds used were 150, 250 and 350 rpm and the dispersed phase volume fractions used were 0.028, 0.02 and 0.01. The following section presents the drop size data obtained using the propeller. The discussion will focus mainly on the comparison of drop sizes obtained for the two impellers. Figure 4.21 shows the evolution of $d_{32}$ at various speeds and for $\phi = 0.028$. 
Figure 4.21: Evolution of $d_{32}$ for the propeller and the Rushton turbine at various impeller speeds, $\phi = 0.028$.

It is evident from Figure 4.20 that the propeller running at 150 and 250 rpm produces similar trends in $d_{32}$ values. Sauter mean drop diameter increases slightly during the initial stages to reach a maximum before decreasing with time. After a significantly long period of time $d_{32}$ value appears to stabilise and remain constant. This trend is consistent with those obtained at 150 and 250 rpm for the Rushton turbine impeller. These trends in $d_{32}$ values at 150 and 250 rpm for both impeller types are different from those reported in the literature (Hong and Lee, 1985; Tsouris and Tavlarides, 1994; Pacek et al, 1999; Baldyga et al, 2001). As discussed earlier, the reason for this unusual trend is due to the changes in viscosity during the experimental run. Figure 4.22 shows the transient viscosity of the dispersion for the case where propeller was used.
Figure 4.22 clearly shows that viscosity of the dispersion increases dramatically with time before reaching a relatively constant value. The rate of increase and the time required to reach the constant value varies slightly with speed. At higher speeds, the rate of increase is the greatest and equilibrium is reached earlier. These trends are similar to those observed for the Rushton turbine (Figure 4.4). Therefore similar reasoning can be used to explain the behaviour of $d_{32}$ results for the propeller at lower speeds. In the initial stages, the breakage rate decreases with increasing $\mu_c$, resulting in an increase of $d_{32}$. Further increase in $\mu_c$, causes the coalescence rate to decrease, resulting in a decrease of $d_{32}$. Any further increase in $\mu_c$ results in a region in which $d_{32}$ remains constant. This occurs because the decrease in the breakage rate is counterbalanced by the decrease in the coalescence rate. At 350 rpm, $d_{32}$ values for the propeller exhibits a trend which is different from those obtained at lower speeds (150 and 250 rpm). The $d_{32}$ appears to remain relatively constant throughout the agitation period or possibly decreasing slightly initially before reaching a constant value. This trend is similar to those observed for the Rushton turbine operating at higher speeds and those in the literature sources such as Hong and Lee (1985), Tsouris and Tavlarides (1994) and Baldyga et al (2001). Therefore similar reasoning can be used to describe the behaviours of $d_{32}$ results for the propeller operating at higher speeds. In these cases, the drop breakage
rate dominates the coalescence rate initially until the equilibrium drop size distribution is achieved. At equilibrium, breakage and coalescence processes occur at the same rate resulting in a constant $d_{32}$ value. Figures 4.23 and 4.24 show the transient behaviour of $d_{32}$ results obtained for propeller and Rushton turbine impeller for $\phi = 0.02$ and $\phi = 0.01$ respectively.

![Figure 4.23: Evolution of $d_{32}$ for the propeller and the Rushton turbine at various impeller speeds, $\phi = 0.02$.](image-url)
The evolution trends of $d_{32}$ for $\phi = 0.02$ (propeller at all speeds) show that the $d_{32}$ increases initially before reaching a relatively constant value. Similar trend is observed for Rushton turbine impeller at 150 rpm and $\phi = 0.02$, and $N > 250$ rpm and $\phi = 0.01$. It appears that the increase in $d_{32}$ at the initial stages is probably a result of the coalescence rates being greater than the breakages rates. As time progresses, the breakage rate probably increases and eventually equals the coalescence rate. This leads to the constant $d_{32}$ value.

The evolution trends of $d_{32}$ for $\phi = 0.01$ with the propeller operating at various speeds show that $d_{32}$ increases continuously throughout the period of agitation. This trend is also observed for the case where $\phi = 0.01$ and $N = 150$ rpm for Rushton turbine impeller. It was argued in the earlier sections that these trends are attributed to the change in viscosity during the dispersion process. Similar arguments can be made for the propeller. It can be seen in Figures 4.25 and 4.26 that the transient viscosity values for the propeller for $\phi = 0.02$ and $\phi = 0.01$ follow trends similar to those obtained for the Rushton turbine.
Figure 4.25: Transient viscosity of the dispersion with the propeller at various impeller speeds, $\phi = 0.02$.

Figure 4.26: Transient viscosity of the dispersion with the propeller at various impeller speeds, $\phi = 0.01$. 
Transient viscosity curves show that the viscosity increases initially and reaches a relatively constant value after a long period of agitation. This trend is observed for all impeller speeds, dispersed phase volume fractions and impeller types. However, the values at which the viscosity stabilises varies with $\phi$. For the propeller, the viscosity stabilises at about 8.5-10 Pa.s for $\phi = 0.028$ and at about 4.5-5.5 Pa.s and 2.5-3.5 Pa.s for $\phi = 0.02$ and 0.01 respectively. These values are comparable with those produced by the Rushton turbine impeller. Although the equilibrium values and transient viscosity trends are similar, there are some notable differences for the two impellers. In the case of the propeller, the viscosity increases rapidly and reaches a constant or equilibrium value within a shorter period of time as compared to that obtained for the Rushton at the same impeller speed and dispersed phase volume fraction. For instance, at $N = 150$ rpm and $\phi = 0.028$, Rushton impeller leads to a curve which shows that the viscosity increases gradually to reach a constant value after a period of more than 2 hours. On the other hand, for the propeller, constant viscosity value is achieved within 20 minutes. As a consequence, the effect of $\mu_C$ on the coalescence and breakage processes will be different for the two impeller types. This in turn would be reflected on the evolution of $d_{32}$. For $N = 150$ rpm and $\phi = 0.028$, the trend in $d_{32}$ values for both impeller types are the same, but the maximum value of $d_{32}$ achieved for the Rushton is much greater than that for the propeller. For some impeller speeds and dispersed phase volume fractions, the evolution of $d_{32}$ values obtained with the two impellers differed quite significantly. For instance, at $N = 350$ rpm and $\phi = 0.02$, the propeller produced a drop size trend where $d_{32}$ increases initially before reaching a constant value after a long period time. On the other hand for the Rushton turbine, the trend is such that $d_{32}$ increases initially, reaches a maximum value and thereafter decreases with time.

It was found that the results obtained with the Rushton have four different evolutionary trends. These four trends are also present in the $d_{32}$ results generated by the propeller. However, the range of operating conditions (dispersed phase volume fraction and impeller speed) in which these are likely to occur differ slightly for the two impeller types. The trends in $d_{32}$ results and the experimental conditions at which they are likely to occur for the propeller are shown below.
Trend 1: \( d_{32} \) decreases at initially and becomes relatively constant with time. It occurs at high \( \phi \) and high \( N \).

Trend 2: \( d_{32} \) increases initially, reaches a maximum and decreases with time (possibly become relatively constant after a long period of agitation). It occurs at high \( \phi \) and low \( N \).

Trend 3: \( d_{32} \) increases at initially before reaching a constant value after a long period of agitation. Modium \( \phi \) at all speeds (\( 150 \leq N \leq 350 \)).

Trend 4: \( d_{32} \) increases continuously with agitation. Low \( \phi \) at all speed (\( 150 \leq N \leq 350 \)).

4.3.2 Evolution of Drop Size Distribution

Figures 4.27-4.29 show the DSD of dispersion at 150 rpm for the three dispersed phase volume fractions used.

![Figure 4.27: Evolution of DSD for the propeller at 150 rpm, \( \phi = 0.028 \).](image)
Figure 4.28: Evolution of DSD for the propeller at 150 rpm, $\phi = 0.02$.

Figure 4.29: Evolution of DSD for the propeller at 150 rpm, $\phi = 0.01$.

Figure 4.27 shows that the DSD is broadening and shifting towards larger sizes initially before narrowing and shifting towards smaller sizes. As time progresses, the rate of change
in the DSD diminishes. As the Figure illustrates, the change in DSD after 2 and 5 hours is minimal. This is an indication of the attainment of steady state DSD. At $\phi = 0.02$, the DSD appears to broaden and shifts towards larger sizes at time progresses. Figure 4.28 shows the DSD changing quite rapidly initially. However, with time, the rate of change in DSD appears to diminish and eventually it becomes relatively constant after a long period of time. The evolution of DSD at $\phi = 0.01$ (Figure 4.29) shows the distribution broadening and shifting towards small drop sizes continuously. This suggests that coalescence rates are much higher than the breakage rate throughout the dispersive process. In contrast to the trend at $\phi = 0.02$, the rate of change in DSD at $\phi = 0.01$ appeared to be fairly constant.

The three dispersed phase volume fractions produced three distinctive evolutionary trends of DSD at 150 rpm. Most other speeds exhibited one of these trends (see Appendix A.6 for remaining cases). The exception was for $\phi = 0.028$ at high speeds, where the DSD appears to narrow slightly and shifts towards small drop sizes with time. Therefore, very much like the evolution of $d_{32}$ which contained four distinctive types of trends, the evolutionary trends of DSD could also be categorised into four types. In fact, the trends in $d_{32}$ values provide an insight into DSD results and vice versa. It can be seen that when $d_{32}$ increases the DSD broadens and shifts towards larger droplets and when $d_{32}$ decreases the DSD narrows and shifts towards smaller sizes. Another observation that can be made is that all drop size distributions are represented by log-normal distribution with tail a peak at the smaller drop size side and a long tail on larger drop size size.

As discussed earlier, the Rushton turbine produces four evolutionary trends of DSD just as the propeller. Another similarity is that both impellers produce distributions which are mainly log-normal. However, the Rushton turbine produces normal distributions for $\phi = 0.028$ at higher impeller speeds.

### 4.3.3 Steady State Drop Sizes

There have been several investigations which studied drop size variation in liquid-liquid systems using several impeller types (Kafarov and Babanov, 1959; Rodriguez et al, 1961; Fernandes and Sharma, 1967; Pacek et al, 1999; Sechremeli et al, 2006). Kafarov and

Kafarov and Babanov (1959) examined the effect of impeller type on the interfacial area in a toluene-water system. They used several impellers including those used in the present investigation, i.e. 6-bladed Rushton turbine and 3-bladed propeller. The latter was deemed to provide larger interfacial area compared to the former. Given the inverse relationship between $d_{32}$ and ‘a’ ($d_{32} = 6\phi/a$), the propeller can be considered to produce larger drops in comparison to the Rushton turbine. This was found to be consistently the case for all the impeller speeds investigated. Rodriguez et al (1961) determined the interfacial area in ethylhexanol-water dispersion using several impellers. Their results suggested that the propeller produces the largest drops at a given impeller speed. The 6-curved bladed turbine has been found to produce the smallest drops, whereas the drops produced by the 6-pitched bladed turbine were found to be larger in comparison. The investigations mentioned above involved relatively high dispersed phase volume fractions, i.e. $\phi = 0.4$ (Kafarov and Babanov, 1959) and $\phi = 0.15$ (Rodriguez et al, 1961). Fernandes and Sharma (1967) determined the interfacial area of a number of liquid-liquid systems using the chemical method. They found that the Rushton turbine produced larger interfacial area than the propeller. All the above three studies certainly imply that the 6-bladed Rushton turbine is more effective in generating larger interfacial area (or producing smaller drop sizes) than the 3-bladed marine propeller. It should be noted that the impeller Reynolds numbers in these studies were high (turbulent regime) which corresponds to a power number $N_{po} = 5$ (Dickey et al, 2001) for Rushton turbine and $N_{po} = 0.9$ (McCabe et al, 1993) for the marine propeller. The higher power number for the Rushton indicates that the turbulence energy dissipation rate per unit mass ($\varepsilon_{\text{max}}$) will be higher for a given impeller speed and thus greater drop breakage and/or smaller coalescence rates (Secheremeli et al, 2006). Given that the drop size distribution in an agitated dispersion is a result of the dynamics that exists between the drop breaking and coalescing processes, greater breakage rate and smaller coalescence rate provided by the Rushton would translate into smaller drop sizes than that for the propeller. However, findings in the present investigation are totally in contrast to the trends found in previous studies. As shown in Figure 4.30, the steady state Sauter mean drop diameter produced by the propeller is smaller than that for the Rushton turbine in equivalent conditions.
For all dispersed phase volume fractions used (0.028 and 0.01 shown in Figure 4.30 and 0.02 in Appendix A.8), steady state $d_{32}$ values for the propeller are smaller than that for the Rushton turbine at all impeller speeds. For instance, at 150 rpm and for $\phi = 0.028$, the Rushton turbine produced a steady state $d_{32}$ value of 89 $\mu$m. $D_{32}$ for the propeller in the same conditions is only 45 $\mu$m. At the higher speed of 350 rpm ($\phi = 0.028$), the difference was much smaller, where $d_{32}$ values are 33 and 23 $\mu$m for the Rushton and propeller respectively.

This trend is opposite to that found in previous investigations which measured drop sizes using the two impellers (Kafarov and Babanov, 1959; Rodriguez et al, 1961 and Fernandes and Sharma, 1967). It should be however noted that the current system operates under laminar conditions in which the drop breakage mechanism is different from that of turbulent conditions prevailed in most of the systems used in previous studies. To explain the behaviour of $d_{32}$ results noted above, the model developed by Kumar et al (1991) may be used. They suggested that the mechanism responsible for drop breakage especially at high $\phi$ values could be the shear in the boundary layer on the blades. Based on this proposition, they developed the following equation for maximum drop diameter $d_{max}$:

![Figure 4.30: Steady state Sauter mean drop diameter, $d_{32}$, versus impeller speed for the propeller and Rushton turbine at various dispersed volume fractions.](image-url)
\[ d_{\text{max}} = \frac{Ca_s \sigma}{113.2 N^{1.2} \mu^{0.8} \left( \frac{1}{L^2 \rho} \right)^{0.2}} \]  

(4.4)

where \( N \) is the impeller speed, and \( L \) is the blade length. The capillary number \( Ca_s \) in equation 4.4 is based on the shear flow of the continuous phase in the boundary layer and is given by:

\[ Ca_s = \frac{\dot{\gamma}_{\text{max}} \mu_e}{2 \sigma} \]  

(4.5)

where \( \dot{\gamma} \) is the shear rate in the boundary layer, \( \mu_e \) is the emulsion viscosity and \( \sigma \) is the interfacial tension. Based on Kumar et al.'s model, it would be expected that impeller with longer blades will produce smaller drop sizes. Both the Rushton turbine and propeller used in this study has the same diameter but the blade length of the former (12.5 mm) is relatively smaller than that of the latter (effective length is 18 mm). Assuming that the shear in the boundary layer influences the drop deformation, it is quite feasible that drops produced by the propeller will be smaller than those produced by the Rushton turbine.

Another interesting trend that could be observed in Figure 4.30 is that the difference in \( d_{32} \) is the greatest at the lowest speed and the difference progressively become smaller with increasing impeller speed. No such results were presented by Rodriguez et al (1961) and Fernandes and Sharma (1967). However, the results produced by Kafarov and Babanov (1959) show that the difference is increasing slightly with increasing impeller speed. This observation suggests that the Rushton have a tendency to increase the breakage rate and/or decrease the coalescence rate with increase in impeller speed much more effectively as compared to the marine propeller.

The difference in drop sizes produced by the two impellers can be better illustrated by the drop size distribution at various operating conditions. Figure 4.31 shows DSD produced by the propeller and the Rushton at 350 rpm (\( \phi = 0.01 \)) and 250 rpm (\( \phi = 0.028 \)).
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Figure 4.31: Steady state DSD for the propeller and the Rushton turbine impeller (a) at 350 rpm for $\phi = 0.01$ (b) at 250 rpm for $\phi = 0.028$.

It is quite clear from the Figures that the distribution produced by the propeller is always narrower and on the smaller drop size side as compared to the distribution obtained with Rushton at the same operating conditions. In other words, for the same dispersed phase volume fraction and rotational speed, the drops produced by the propeller are smaller than the
ones produced by the Rushton turbine. This trend is observed in all experimental conditions (Appendix A.8).

4.3.4 Steady State $d_{32}$ for the Propeller at Various N and $\phi$

The relationship between steady state $d_{32}$ and the propeller operating at various speeds is shown in Figure 4.32. It can be seen that $d_{32}$ progressively decreases with impeller speed for all dispersed phase volume fractions. The inverse relationship between $d_{32}$ and N was also reported by Kafarov and Babanov (1959), the only other investigation that presented such results using the marine propeller. In addition, several other studies produced similar results using impellers other than the commonly used 6-bladed Rushton turbine. Zhou and Kresta (1998b) and Pacek et al (1999) used several impeller types including some with low power numbers and high flow numbers similar to the marine propeller, and Sechremeli et al (2006) employed open bladed impellers to provide agitation. However, all these investigations were conducted in turbulent conditions as opposed to the present study which operated in the laminar regime. Nevertheless, in all these cases, the inverse relationship between $d_{32}$ and N seems to hold irrespective of the design of the impeller.

![Figure 4.32: Log-log plot of steady state Sauter mean drop diameter, $d_{32}^*$ versus impeller speed, N for the propeller at various dispersed phase volume fractions.](image-url)
The plot of \( d_{32} \) versus \( N \) on a log-log graph shows good correlations for all dispersed phase volume fractions. The \( R^2 \) values for these cases are in excess of 0.99, indicating strong agreement between the two parameters. The linear relationship has also been found in most investigations which used Rushton turbine impeller in turbulent flow conditions (Roger et al., 1956; Bouyatiotis and Thornton, 1967; Weinstein and Treybal, 1973; Okufi et al., 1990; Gallego-Lizon and Perez de Ortiz, 2000) and in laminar and/or transitional flow (Stamatoudis and Tavlarides, 1985). In addition, the linear fit was deemed to be the most appropriate for the results produced by the Rushton turbine in the present investigation. Several drop sizes studies which used impellers other than the Rushton turbine (Kafarov and Babanov, 1959; Scheremeli et al.; 2006; Pacek et al., 1999) also produced similar results.

The straight line fit to the plots of \( d_{32} \) versus \( N \) in Figure 4.32 have slopes of -0.47, -0.63 and -0.77 for dispersed phase volume fractions 0.01, 0.02 and 0.028 respectively. These slopes are significantly smaller than those obtained for the Rushton turbine. In fact, the slopes of best fit lines for the Rushton turbine are 70% greater than those for the propeller. This suggests that a variation in impeller speed has greater impact on steady state drop sizes with the Rushton turbine as compared to the propeller. It is also evident that the gradient of the best fit lines progressively increases with increasing \( \phi \) which is a trend different from that for the Rushton turbine. The Rushton turbine produced a trend where the slope decreases with increasing \( \phi \) to reach a minimum before increasing. Stamatoudis and Tavlarides (1985) suggested that the variation in \( \mu_C \) has an effect on the relationship between \( d_{32} \) and \( N \) for the Rushton turbine. Despite having similar variation in \( \mu_C \), results produced by the propeller are different from those for the Rushton turbine. The trend observed with the propeller is more consistent with those observed by Sechremeli et al (2006) for a Rushton turbine and an open type impeller. This is despite the fact that the above mentioned study was conducted with constant viscosity.

Influence of \( \phi \) on the steady state \( d_{32} \) is shown in Figure 4.33 for the propeller. The plot shows that an increase in \( \phi \) results in a decrease in \( d_{32} \). This could be attributed to the variable steady state \( \mu_C \) that is associated with \( \phi \) (Figure 4.22, 4.25 - 4.26). As with the Rushton turbine, propeller produces results in which \( \mu_C \) increases with \( \phi \). Dokie-Baucal et al
Ludwig et al. (1997) and Fernandes and Sharma (1967) found that an increase in $\mu_C$ generally leads to a decrease in $d_{32}$.

Most of the investigations which examined the effect of $\phi$ on $d_{32}$ found that these two parameters are directly proportional to each other (Brown and Pitt, 1970; Colulaloglou and Tavalarides, 1976; Mlynek and Resnick, 1972; Okufi et al., 1990). Unlike previous investigations, the present study involves variation in both $\phi$ and $\mu_C$. Given that $\phi$ and $\mu_C$ have opposing effects on $d_{32}$, the trends depicted in Figure 4.33 suggest that the $\mu_C$ has the greater influence on the evolution of $d_{32}$. The best fit curves for $\phi$ versus $d_{32}$ data show fairly good agreement ($R^2 > 0.97$). As in the case for the Rushton turbine, the slopes of the best fit lines appear to decrease with impeller speed. This indicates that the combined effect of $\mu_C$ and $\phi$ decreases gradually with increasing impeller speed.

![Figure 4.33: Steady state Sauter mean drop diameter, $d_{32}^*$ versus dispersed phase volume fractions, $\phi$ at various impeller speeds for the propeller.](image)
4.3.5 Steady State DSD of the Propeller at Various N and φ

The influence of impeller speed on steady state drop size distribution at dispersed phase volume fractions of 0.028 is shown in Figure 4.34 for the propeller (DSD at φ = 0.01 and 0.02 are presented in Appendix A.7). It is evident from the plot that an increase in impeller speed results in narrowing of the distribution and a shift towards smaller sizes. This trend was also observed with the Rushton turbine in the present investigation as well in previous investigations which used the Rushton turbine (Gallego-Lizon and Perez de Ortiz, 2000; Okufi et al, 1990; Schulze et al, 2000). Zhou and Kresta (1998) found that several impellers other than the Rushton turbine also produced results where DSD curve narrows as N is increased. It can be seen that the distributions produced by the propeller are primarily log-normal with a tail towards larger drops sizes. However, there is a slight indication of DSD becoming normal distribution as the impeller speed is increased.

![Figure 4.34: Steady state DSD for the propeller at various impeller speeds, φ = 0.028.](image-url)
Figure 4.35: Steady state DSD for the propeller at various dispersed phase volume fractions, N = 150 rpm.

Figure 4.35 shows the influence of $\phi$ on DSD at 150 rpm for the propeller. These results clearly show that the distribution becomes narrower and shifts towards smaller sizes with increasing $\phi$. This trend is similar to those found at other speeds (Appendix A.7) and those for the Rushton turbine. However, this trend is in contrast to those found by other investigators (Okufi et al., 1990; Kraume et al., 2004) where DSD broadens and shifts towards larger sizes as dispersed phase volume fraction increases. The contrasting trends observed in the present investigation could be attributed to the increase in $\mu_C$ which increased with increase in $\phi$. Stamatoudis and Tavlarides (1985) and Noro (1978) found that an increase in $\mu_C$ results in a narrowing of DSD and a shift towards smaller sizes. Thus it is quite feasible that the DSD trends observed with the propeller is a result of the variation in the continuous phase viscosity as it was for the Rushton turbine.
4.4 Prediction of Sauter Mean Drop Diameter

There are numerous empirical and semi-empirical correlations that have been developed to predict drop sizes in liquid-liquid systems. However, there are no correlations that can confidently be used to predict the \(d_{32}\) outside the range of conditions at which they were tested. Furthermore, majority of the correlations published have been for fully turbulent conditions \((N_{Re} > 10^4)\), particularly dilute systems, where coalescence can be neglected. The present system however, operates in the laminar to low transitional regime. Despite the scarcity of dispersive studies in such conditions there have been some correlations that have been developed from the fundamentals of single drop breakage. With the exception of handful of investigations (Wichterle, 1995; Shimizu et al, 1999; Pacek et al, 2001), dispersed phase drops have not been fitted using these correlations. To the authors’ best knowledge, no reactive liquid-liquid system (in non-turbulent regime) has been examined in such a manner. The following section will attempt to fit the steady state Sauter mean drop diameter using several of these models and determine the most suitable one to predict drop sizes in the present system.

Correlation proposed by Pacek et al (2001) is as follows:

\[
Ca_{cr} = \left[\frac{d_{max}}{2}\right] k_s N \mu_C \frac{N_{kd}}{\sigma} \tag{4.6}
\]

where \(Ca_{cr}\) = critical capillary number
ks = Shear rate constant
N = impeller speed, rps
\(\sigma\) = interfacial tension, N/m
\(\mu_C\) = continuous phase viscosity, N.s/m²
\(d_{max}\) = maximum stable drop diameter, m
There have been considerable experimental evidences to suggest that the maximum stable drop diameter, $d_{\text{max}}$ is proportional to $d_{32}$ ($d_{32} = C d_{\text{max}}$). Values of the constant, $C$ have been shown to vary according to the operating conditions used in the studies (Table 2.1). However, these studies have been conducted in fully turbulent conditions and therefore the application of these relationships to laminar condition is yet to be determined. Nevertheless one must assume a proportionality in order to fit the drop size data obtained in the present system. Therefore it is assumed that $d_{32}$ is directly proportional to $d_{\text{max}}$. The shear rate constant, $k_s$ for 6-bladed Rushton turbine is taken as 11.5 (Harnby et al, 1992). Several authors have produced curves of capillary number, $C_{a_{\text{cr}}}$ as a function of the viscosity ratio, $\mu_d/\mu_c$ (Karam and Bellenger, 1968; Grace, 1982). The curve produced by Grace (1982) (Figure 2.11) is used to determine $C_{a_{\text{cr}}}$ in the present study.

The present experimental study examined the effects of impeller speed and dispersed phase volume fractions on $d_{32}$, producing 14 different steady state $d_{32}$ values. $D_{32}$ values were predicted using the equation 4.6 and it was found that the calculated values were uniformly greater than the experimental values. The reason for this could be that assumption $d_{32} = d_{\text{max}}$ maybe invalid for this particular system. As there is no precedent for such a study under laminar conditions, it is difficult to determine whether the above assumption is valid for the present case. In order rectify the variance, a multiplier (or constant) was applied to the correlation. The constant was obtained by curve fitting and was found to be 0.21.

Figure 4.36 shows the comparison between the experimental $d_{32}$ values and those calculated from equation 4.6 modified with the constant (0.21).
The correlation coefficient, $R^2$ is found to be equal to 0.88, indicating that the calculated and experimental values agree fairly well. However, the calculated values appear to overpredict experimental values for smaller drops and underpredict for larger drops. The correlation could be improved with further modification of the equation 4.6. According to the equation, the functionality between $d_{32}$ and the impeller speed is $d_{32} = N^{-1}$. This is different from what have been observed in the experimental results. Figure 4.15 shows the exponent of $N$ were -1.19, -1.31 and -1.07 for dispersed phase volume fractions 0.01, 0.02 and 0.028 respectively. The average value of these exponents would be -1.2. This value is equivalent to that used in most drop size correlations developed for turbulent liquid-liquid dispersion. Incidentally such relationship appears to hold good for this particular system despite it is operating in the laminar regime. Therefore, the exponent of -1.2 was incorporated in equation 4.6. It was further modified with the addition of a constant to produce the following correlation for predicting the steady state Sauter mean drop diameter:

$$d_{32} = \frac{0.53C_{a_e} \sigma}{\mu_k \gamma N^{1.2}}$$  \hspace{1cm} (4.7)
It should be noted that the constant (which equalled 0.27) was found by curved fitting and is incorporated into equation (4.6). The experimental values of $d_{32}$ and those calculated using equation 4.7 are compared in Figure 4.37. Results show that there is a fairly good agreement between the experimental and calculated values. The correlation coefficient, $R^2 = 0.89$ which is slightly greater than that for the previous set of results. Furthermore the plot indicates that the difference between the calculated and experimental $d_{32}$ values is fairly uniform throughout the range of $d_{32}$ values. The discrepancies that exist in the comparison could be a result of several factors. The experimental results used for this analysis were essentially the final $d_{32}$ values rather than the actual steady state $d_{32}$ values. Given the reactive nature of the system, the drops were not in the system for a long enough period to reach steady state. This is quite evident from the $d_{32}$ evolution curves depicted in previous sections. In some cases $d_{32}$ continues to vary until the final sampling time (Figure 4.1, 4.5 and 4.6). Furthermore the original correlation itself was developed for non reactive liquid-liquid system, hence it is unlikely to deal with the added complexities of the reaction.

![Figure 4.37: Comparison of experimental steady state $d_{32}$ and those calculated from equation 4.7.](image-url)
Based on the shear breakup in the boundary layer on the impeller blade, Kumar et al (1991) proposed a correlation to predict drop sizes in liquid-liquid systems. Improvement of the correlation was later published in Kumar et al (1998). The main purpose of their development was to predict the behaviour of drops in turbulent flow at high dispersed phase volume fractions. Given its basis is on the shear breakup suggests that it could be suitable for predicting drop sizes in laminar conditions. The correlation produced in Kumar et al (1998) is as follows:

$$d_{\text{max}} = \frac{Ca(\lambda)\sigma}{15.4N^{1.2}\mu\left(\frac{\mu}{L^2\rho}\right)^{0.2}}$$

(4.8)

where $Ca_{cr}$ = critical capillary number

$N$ = impeller speed, rps

$\rho$ = density, kg/m$^3$

$\lambda$ = viscosity ratio ($\mu_d/\mu_c$)

$L$ = impeller blade length, m

$\sigma$ = interfacial tension, N/m

$\mu$ = viscosity, N.s/m$^2$

Critical capillary numbers were obtained from Grace (1982). To fit the $d_{32}$ data in the present study the equation was modified with the addition of a constant to produce the following expression:

$$d_{32} = \frac{4.03Ca(\lambda)\sigma}{N^{1.2}\mu\left(\frac{\mu}{L^2\rho}\right)^{0.2}}$$

(4.9)

It should be noted that the constant (which equalled 62) was found by curved fitting and is incorporated into equation (4.9). The steady state Sauter mean drop diameters calculated from equation 4.9 are compared to experimental values in Figure 4.38. The correlation coefficient, $R^2 = 0.93$ suggests a good agreement between the calculated and experimental $d_{32}$ values.
The calculated values generally appear to underpredict the experimental values. There are several sources of error that could be the reason for this difference. Due to the reactive nature of the present system, steady state may have not been achieved. Also the exponent of N in equation 4.9 was taken as -1.2 which is an average value that does not accurately reflect the relationship between \( d_{32} \) and N for all three dispersed phase volume fractions.

![Graph showing comparison of experimental steady state \( d_{32} \) and those calculated from equation 4.9.](image)

*Figure 4.38: Comparison of experimental steady state \( d_{32} \) and those calculated from equation 4.9.*

It has been shown that the modified versions of the correlations developed by Pacek *et al* (2001) and Kumer *et al* (1998) are able to predict \( d_{32} \) values fairly well. The latter showed better predictive capability as indicated by the higher \( R^2 \) value. The data used in the development correlations are for the 6-bladed Ruhston turbine impeller. The following section shows an attempt to fit the \( d_{32} \) data for the propeller with correlations developed by Pacek *et al* (2001) and Kumer *et al* (1998). Figure 4.39 compares the calculated \( d_{32} \) values using Kumar *et al* (1998)’s correlation with the experimental values.
Chapter 4

It is clear from the correlation coefficient \( R^2 = 0.70 \) that there is a large discrepancy between the calculated and experimental values. The reason could be due to the fact that the relationship between \( d_{32} \) and impeller speed in equation 4.8 varies significantly from those observed in the experiments. The observed exponents are -0.47, -0.63 and -0.77 for dispersed phase volume fractions 0.01, 0.02 and 0.028 respectively. In order to improve the correlation the equation 4.9 was modified by incorporating the average value of these exponents. Figure 4.40 depicts the experimental \( d_{32} \) and those calculated from the modified version of the correlation developed by Kumar et al (1998). The modified equation is as follows:

\[
d_{32} = \frac{1.33Ca(\lambda)\sigma}{N^{0.62}} \left( \frac{\mu}{L^2\rho} \right)^{0.2}
\] (4.10)

It should be noted that the above equation incorporates a constant (which equalled 20.5) that was found by curved fitting.
The correlation coefficient, $R^2 = 0.95$ in Figure 4.40 is a clear indication of significant improvement in the correlation between the calculated and experimental values. It appears that the modified equation has been quite successful in predicting $d_{32}$ values obtained using the propeller. It should be noted that in addition to the modification of the exponent of $N$, equation 4.10 also contains a multiplier or constant. This is necessary to alleviate uniform discrepancies that existed between experimental and calculated $d_{32}$ values. Attempts were made to fit the propeller data to equation developed by Pacek et al (2001). However results showed very little agreement between experimental and calculated results (Appendix A.9). Calculated values from equation 4.6 and experimental value produced a correlation coefficient of 0.58. The equation was modified with a new exponent of $N$ (-0.62) producing a correlation coefficient of 0.69. Therefore it can be concluded that propeller results can be better predicted from the correlation developed by Kumar et al (1998) as compared to that of Pacek et al (2001).
This chapter presents and discusses the results produced by reactant concentration experiments. Reactant conversion rates at various impeller speeds and impeller types are subject to discussion. Time variant dispersed phase volume fraction and interfacial area results are also included. In addition, the chapter presents a model to predict transient interfacial area of the liquid-liquid system.
5.0 Introduction

The liquid-liquid system used in the present investigation is categorised as a liquid-liquid heterogeneous reaction. It involves the reaction of two components present in two distinctive phases, i.e. PIBSA (continuous phase) and MEA (dispersed phase). The reactive scheme is:

\[ \text{PIBSA} + \text{MEA} \rightarrow \text{PIBSA derivative emulsifier} \]

Figure 5.1: Reaction scheme that represents the formation the PIBSA derivative emulsifier.

Heterogenous reactive systems are complicated by the fact that two processes, chemical reaction and mass transfer, occur simultaneously. The system is further complicated by the fact that these processes interact and the overall conversion rate can be expressed as ((Levenspiel, 1979):

\[ r = \frac{C_B}{1 + \frac{H_A}{k_d a} + \frac{H_A}{k_C a l C_A}} \]  

(5.1)

where  
\( r \) = rate of formation of products, mol/s  
\( k \) = second order rate constant, m³/mol.s  
\( C_A \) = bulk concentration of A, mol/m³  
\( C_B \) = bulk concentration of B, mol/m³  
\( l \) = volume fraction of the phase within which A and B reacts (for this
particular system, the continuous phase)
a = interfacial area, m²/m³

\(k_d\) = dispersed phase mass transfer coefficient, m/s

\(k_c\) = continuous phase mass transfer coefficient, m/s

\(H_A\) = distribution coefficient

The overall rate equation contains several components including dispersed phase and continuous phase mass transfer coefficient, distribution coefficient, reaction rate constant and interfacial area. Each of these components is affected by a number of variables including operating conditions, physical properties of the system and vessel geometry. To the authors’ best knowledge, the components (in equation 5.1) for the present system have not been subjected to investigation previously. The present study will focus on the effect of impeller speed, impeller type and dispersed phase volume fraction on reactant conversion rates. In addition, the effect of the above mentioned variables on the interfacial area will also be examined.

The reaction conversion rate was determined by measuring the concentration of PIBSA using Fourier transform infrared spectroscopy with a 50 µm NaCl fixed pathlength solution cell. The experimental procedure and equipment are detailed in Chapter 3. Although all the planned experiments were conducted, reasonable results were obtained only for a limited range of experimental conditions. The technique adopted for this study was not able to produce results at conversion levels above 80 ± 5%. In many cases, the upper limit of conversion was reached too quickly and as such conversion rates could not be established. Nevertheless some reaction data was obtained and these are presented in the following sections.
5.1 Conversion Rates

5.1.1 Effect of Impeller Speed and Dispersed Phase Volume Fraction

The conversion of the reactant, PIBSA, with respect to time is presented in Figure 5.2. The initial volume fraction of the dispersed phase, MEA was 0.028. The Figure presents conversion data at several impeller speeds ranging from 150 to 450 rpm. It is clear that PIBSA is converted at an exponential rate at all speeds. The fractional conversion curves exhibit a trend in which the gradients gradually decreases with time.

![Figure 5.2: Transient conversion fraction of PIBSA for the Rushton turbine impeller at various speeds, \( \phi = 0.028 \).](image)

The results shown in Figure 5.2 also indicate that the rate of conversion is a function of the impeller speed. At the lowest speed of 150 rpm, the rate of conversion is lower than that of higher speeds at all time intervals. On the other hand, the highest speed, 450 rpm produces the greatest conversion rate. Thus it could be stated that the conversion rate increases with increasing impeller speed. Table 5.1 shows the time required to achieve 80% conversion (or 0.80 fractional conversion) of PIBSA at various impeller speeds.
Table 5.1: Time required reach 80% conversion at various speeds (Rushton)

<table>
<thead>
<tr>
<th>Speed (rpm)</th>
<th>Time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>33</td>
</tr>
<tr>
<td>250</td>
<td>13</td>
</tr>
<tr>
<td>350</td>
<td>8</td>
</tr>
<tr>
<td>450</td>
<td>2.5</td>
</tr>
</tbody>
</table>

At 450 rpm, 80% conversion is achieved within 2.5 minutes (150 seconds), whereas at 150 rpm, it takes approximately 33 minutes to achieve the same level of conversion. At 250 rpm and 350 rpm, 80% conversion is achieved in approximately 13 and 8 minutes respectively. Although not presented in figure 5.2, an experiment was also conducted at an impeller speed of 600 rpm. Results produced in the experiment showed that 80% conversion was achieved even before the first sample time of 2 minutes. Consequently, a conversion trend could not be established. However, the result does reinforce the notion that higher the speed, greater the conversion rate.

As discussed in the earlier chapter, drop size measurements were conducted for a range of dispersed phase volume fractions. Similarly, attempts were made to determine the reactant conversion rates using the dispersed phase volume fractions of 0.01 and 0.02. However, meaningful results in terms conversion rate could not be obtained. It was found that the maximum possible conversion is achieved even before the first sample time of 2 minutes. The results in Figure 5.3 show that the conversions of 32% and 71% are achieved with the dispersed phase volume fractions of 0.01 and 0.02 respectively. Although these results do not produce sufficient information to determine the trend of conversion rates, the results do indicate that the assumption of equimolar stoichiometry is valid for this reaction. According to the calculations shown in Appendix A.10, equimolar reaction for a dispersed phase volume fraction of 0.01 and 0.02 would produce conversions of 35.6% and 71.2% respectively. These results are comparable to the experimental results obtained.
5.1.2 Effect of Impeller Type

Results discussed in the previous section were obtained using the 6-bladed Rushton turbine impeller. To examine the effect of impeller type on conversion, similar experiments were conducted using the 3-bladed marine propeller. Results obtained using the propeller and those of comparable speeds for the Rushton turbine are presented in Figure 5.4.
It is evident from the curves depicted in Figure 5.4 that conversion of PIBSA occurs at exponential rate for both impeller speeds examined. Experiments were also conducted using higher impeller speeds (N > 250) however results were as such that the conversion limits were reached within the first sampling time of 2 minutes. Thus a complete trend of conversion rates could not be established. This is also the case at 250 rpm, but the result can be used for comparative purposes. For instance, at 150 rpm 80% conversion is achieved 8 minutes after the commencement of the reaction, whereas at 250 rpm this is achieved within 2 minutes. This clearly indicates that the conversion rate at 250 rpm is greater than that at 150 rpm. The trend of conversion rate increasing with increasing impeller speed is also found for the Rushton turbine.

Comparing the two impeller types in terms of conversion rates, it is apparent that the propeller produces greater conversion rates compared to the Rushton turbine. At 150 rpm, the Rushton turbine produces 80% conversion in 33 minutes which is much longer than the 8 minutes it takes for the propeller to produce the same level of conversion. Similar trend is found for the case of 250 rpm, where 80% conversion is achieved in 13 minutes and within 2 minutes for the Rushton turbine and the propeller, respectively. Therefore, in terms of
conversion rates it appears that the propeller performs better than Rushton turbine for the present system. The main reason for this would be fact that the propeller produces significantly smaller drops as compared to the Rushton turbine (Figure 4.21). It is well established that smaller drop sizes promotes greater conversion rates because they offer larger interfacial area per unit volume.

5.2 Interfacial Area

There are two factors that affect the calculated values of interfacial area, dispersed phase volume fraction ($\phi$) and Sauter mean drop diameter ($d_{32}$). Interfacial area ‘a’ can be calculated using the relationship:

$$a = \frac{6\phi}{d_{32}}.$$  \hspace{1cm} (5.2)

In the previous section of this chapter, conversion rates of PIBSA are presented. Assuming equimolar reaction, these results can be used to calculate time variant dispersed phase volume fraction. Figure 5.5 shows the transient dispersed phase volume fraction for the Rushton operating at various impeller speeds.
The results show that the $\phi$ decreases continuously from the initial value of 0.028 for all impeller speeds examined. The sensitivity of the chemical analysis technique was such that it was only able to produce data based on a certain level of reactant concentration and for a relatively short period of time. Nevertheless clear trends can be observed in the results. Coinciding with the conversion results, the rate of decrease in dispersed phase volume fraction varies with time and impeller speed. Figure 5.5 clearly shows the rate of decrease in dispersed phase volume fraction decreases with time.

To obtain time variant interfacial area, the $\phi$ values shown in Figure 5.5 and drop size data presented in chapter 4 were used. The change in interfacial area with time at four different agitation speeds for Rushton turbine is shown in Figure 5.6. It is clear that the interfacial area decreases continuously with time to reach value zero. This trend is common to all speeds.
In a non-reactive liquid-liquid system, given the inverse relationship between the interfacial area and $d_{32}$, and the fact that $\phi$ remains constant, one would expect that the interfacial area to increase continuously with time before reaching relatively a constant value. However, the present study involves a reactive system. As shown in Figure 5.5, the dispersed phase volume fraction decreases as the reactive component in the phase (MEA) is consumed by the reaction. Considering the relationship between the interfacial area and $\phi$, the decrease in $\phi$ values would result in proportional decrease the interfacial area. The transient trends of interfacial area shown in Figure 5.6 suggest that the effect of $\phi$ on the interfacial area is dominant as compared to that of $d_{32}$. This is especially obvious in the initial stages of the reaction where the interfacial area continues to decrease despite the decrease in $d_{32}$.

The trend of decreasing interfacial area with time is common in all cases shown here, but the rate at which this occurs vary with the impeller speed. At 150 rpm, the interfacial area decreases at a lower rate as compared to those at higher speeds (250, 350 and 450 rpm). In fact, the rate of decrease gradually increases with the increase in impeller speeds. The decrease in the interfacial area is so dramatic at 450 rpm, that the interfacial area becomes virtually zero within 10 minutes. On the other hand at 150 rpm, the interfacial area is reduced to zero only after period of more than 2 hours. Figure 4.1 shows the transient $d_{32}$ values progressively decreasing with the increase in impeller speeds. Considering the relationship between ‘$a$’ and $d_{32}$, the interfacial area in a non reactive system is expected to be lower at lower speeds. However, in the present reactive system, the interfacial area is found to be consistently higher at lower speeds. This finding further reinforces the suggestion that the dispersed phase volume fraction has a dominant effect on the interfacial area in the present system compared to that by $d_{32}$.

The effect of impeller type on the transient interfacial area is also examined. Results produced by the Rushton turbine and propeller operating at 150 and 250 rpm are used for the comparison. Transient dispersed phase volume fraction for the cases are shown in Figure 5.7. Similar to the Rushton turbine, the propeller produced results where the rate of decrease in dispersed phase volume fraction increases with the impeller speed and decreases with time. Comparing the results for the two impellers, it is evident that the propeller leads to a greater rate of decrease in dispersed phase volume fraction as compared to the Rushton in both speeds examined.
Figure 5.7: Transient dispersed phase volume fraction, $\phi$ for the propeller and the Rushton turbine impeller at 150 and 250 rpm, where the initial $\phi = 0.028$. 
Figure 5.8: Transient interfacial area for the propeller and the Rushton turbine impeller at 150 and 250 rpm, where the initial $\phi = 0.028$.

Figure 5.8 compares the transient interfacial area produced by the two impellers at 150 and 250 rpm. It is evident that the transient interfacial area for the propeller follows trends similar to those for the Rushton. The interfacial area decreases with time for all speeds for both impeller types. Comparing the two impeller speeds for the propeller, it is clear that rate of decrease in the interfacial area increases with increase in impeller speed. This is consistent with the trend observed for the Rushton turbine. This is expected given that $\phi$ vs time and $d_{32}$ vs time for the propeller follow trends similar to those for the Rushton turbine.

Comparison of the two impeller types in Figure 5.8 shows that propeller produces lower interfacial areas at a given speed and time. The propeller at 250 rpm has the most dramatic decrease in interfacial areas as compared to those for other cases. In fact, the rate of decrease in interfacial areas is significantly greater for propeller at both 150 and 250 rpm. This is despite the fact propeller produced significantly smaller $d_{32}$ values compared to the Rushton turbine at the respective impeller speeds (Figure 4.21). In general, it appears that the tendency for the Sauter mean drop size to increase the interfacial area is overwhelmed by the effect of the dispersed phase volume fraction.

### 5.3 Correlation for Predicting Interfacial Area

Interfacial area is an important component in the overall reaction rate equation. As such development of a mathematical model for predicting interfacial area is essential for the reactor design. Given the relationship between drop size and interfacial area ($a = 6\phi/d_{32}$), predicting interfacial area from $d_{32}$ correlation can be simple task if two liquid phase are non reactive. In such a case the dispersed phase volume fraction remains constant throughout the dispersive process and the interfacial area can be predicted easily if a reasonable correlation to predict $d_{32}$ is available. However, when there’s a reaction between the two phases the task is more complicated due to the fact that dispersed phase volume fraction varies with time. For instance, in the present investigation the amount of MEA (dispersed phase) present in the
reactor is progressively decreases with time due to its consumption in the reaction. Therefore one would require a model to determine the amount of dispersed phase present as a function of time. The following section will attempt to develop a correlation to predict the transient dispersed phase volume fraction for the present system.

As discussed in sections 5.1, only a limited range of experiments were able to produce reasonable reactant concentration data. Time variant dispersed phase volume fractions were presented in Figure 5.5 for the Rushton turbine and in Figure 5.7 for the propeller. It is clear from these results that dispersed phase volume fraction decreases from an initial value, $\phi_i$ of 0.028. Function that best describes the trend would be an exponential decay having the general form $y = Ae^{-bx}$ or more specifically $\phi = \phi_ie^{-bt}$. It is also noticeable that the impeller speed has an influence on the rate of reduction of the dispersed phase volume fraction. Therefore the effect of the impeller speed must be factored into the overall model. Suitability of several functions were examined and the most appropriate one was found to be power model ($y = Cx^d$). Introducing the functionality of N into the overall model would produce the following expression:

$$\phi = \phi_ie^{-ctN^d} \quad (5.3)$$

The constants c and d were determined using the experimental data using least squares method. Final model for predicting the time variant dispersed phase volume fraction is as follows:

$$\phi = \phi_i e^{-2 \times 10^{-6} tN^2} \quad (5.4)$$

Comparison between the model estimation and experimental data is shown in Figure 5.9. The data points represent the experimental values and the dashed lines represent the values calculated by equation 5.4. Correlation coefficient, $R^2 = 0.95$ suggests that there is a good agreement between the experimental values and those calculated from the model.
Using the model equation to predict time variant dispersed phase volume fraction and $d_{32}$, a model to predict interfacial area can be established. It should be noted that dispersed phase volume fraction model was established for experiments conducted using Rushton turbine impeller at initial dispersed phase volume fraction of 0.028. The associated equation for $d_{32}$ would be equation 4.9. Combining these two equations, the following equation for the interfacial area was obtained:

$$
\begin{align*}
\lambda & = 1.49 \times 10^{-2} N^{1.2} \mu \phi e^{-2 \times 10^{-6} \mu N^2} \\

\text{Ca} (\lambda) \sigma \left( \frac{\mu}{L^2 \rho} \right)^{0.2}
\end{align*}
$$

(5.5)

To determine the validity of the model, comparisons must be made between the value calculated using equation 5.5 and the experimental results. This is a difficult task due to the
limited number of data point available for comparison. Drop sizes were measurable only after certain amount of reactant has been converted and reactant concentration was measurable only upto certain level of conversion. As such only limited numbers of data points are available for interfacial area calculation and these were compared with the model (equation 5.5) in Figure 5.10.

![Figure 5.10: Comparison of experimental results of transient interfacial area with the model, equation 5.5.](image)

The data points represent the experimental values and the dashed lines represent the values calculated by equation 5.5. Figure 5.10 shows the interfacial area obtained from experiments as symbols and the dashed lines are the prediction of equation 5.4. The interfacial area calculated using equation 5.4 starts from a relatively high value and decreases with time. Initial interfacial area at the highest speed corresponds to the highest value. Furthermore, the rate of decrease in the interfacial area increases with increasing impeller speed. At highest speed (450 rpm), the rate of decrease in interfacial area is such that despite having a higher initial value, after a period time the interfacial area is reduced to a much lower value as compared to those calculated for lower speeds. Correlation between experimental values and those calculated from the model is very poor as indicated by the low value of the correlation coefficient ($R^2 = 0.29$). The model appears to overpredict the experimental values. Primary
reason for this is the difference between the experimental and those calculated using equation 4.9. The correlation for \( d_{32} \) was developed from constant or steady state \( d_{32} \) values. Experimental results show that \( d_{32} \) values follow certain evolutionary patterns and do not remain constant throughout the experimental run. Figure 4.1 shows that at the initial times \( d_{32} \) values are generally larger than those at steady state. Given the relationship between the interfacial area and \( d_{32} \), this would result in lower values of interfacial area than those predicted by the model. Another source of error could arise from the relationship between \( N \) and \( d_{32} \) in the drop size correlation. The exponent for \( N \) in equation 4.9 is -1.2, the average value for three dispersed phase volume fractions. As shown in Figure 4.38 this produced fairly good correlation with all the Rushton turbine experimental results. However, the correlation could be improved further if an individual correlation is developed for each dispersed phase volume fraction. Based on experimental results (Figure 4.15), the functionality of \( N \) for \( \phi_i = 0.028 \) would be \( d_{32} \propto N^{-1.07} \). Modifying the \( d_{32} \) correlation with new functionality resulted in a slightly varied expression:

\[
d_{32} = \frac{4.74 Ca(\lambda)\sigma}{N^{1.07}} \left( \frac{\mu}{L^2\rho} \right)^{0.2}
\]

\[\text{(5.6)}\]

Incorporating equation 5.6 with the expression for predicting the interfacial area produced the following model:

\[
a = \frac{1.26 N^{1.07} \mu \phi_i e^{-2\times10^{-6} iN^2}}{Ca(\lambda)\sigma \left( \frac{\mu}{L^2\rho} \right)^{0.2}}
\]

\[\text{(5.7)}\]

Figure 5.11 compares the experimental results with those calculated using equation 5.7. The correlation coefficient, \( R^2 = 0.81 \) suggests that the new model predictions are much improved as compared to those for the previous equation 5.6. Despite the relatively good agreement, some experimental data points still fall slightly below the predictions of the model. This is probably due to the reason that the steady state \( d_{32} \) values are somewhat smaller than the
experimental d_{32} values at initial stages (Figure 4.1). Nevertheless this model appears to be a reasonable approximation of the transient interfacial area observed in the present system. This is a somewhat tentative statement given that only a small number of data points are available for the analysis. Improvement in experimental techniques would broaden the range of measurements that can be made and could give greater credence to the model. Additional data for the propeller and other dispersed phase volume fractions could also result in a more comprehensive model for predicting the time variant interfacial area. Such model could be extended to predict time variant interfacial area in other agitated liquid-liquid reactive systems. The constants and some exponents are required to be modified in accordance with experimental results produced by the study. With respect to present investigation, a model to predict the volumetric mass transfer coefficient, k_{L,a} would be ideal, especially given that it is the main component that encompasses liquid-liquid reactions. However, in order to achieve this, sensitivity of the chemical analysis technique needs to be improved substantially.

![Graph showing transient interfacial area comparison](image)

**Figure 5.11:** Comparison of experimental results of transient interfacial area with the model, equation 5.7.
5.3 Reactor Design Considerations

Development of a mathematical model for predicting the interfacial area is an important element in the development of the overall rate equation. However equation 5.1 contains other components including the reaction rate constant, continuous phase and dispersed phase mass transfer coefficients and distribution coefficient. Quantitative information on these components would be required to determine the production rate and ultimately the reactor design. Experiments conducted during the present investigation did not provide all the information that is required to produce the reactor design equation, but it did provide some useful information on certain aspects of emulsifier production and reactor design.

Two impeller types were used in the present investigation: 6-bladed Rushton turbine and 3-bladed marine propeller. Comparison of the results produced by the two impellers gave an indication of the type impeller that is suitable for the reactor. Conversion results showed that the conversion rate achieved by the propeller is at least four times greater than that achieved by the Rushton turbine (Figure 5.4). Such result is a clear indication of the suitability of the propeller over the Rushton turbine for the present system. Drop size results reinforce this suggestion. Smaller drops promote conversion because they offer larger interfacial area per unit volume. The propeller produced significantly smaller drops as compared to the Rushton turbine (Figure 4.21). This is totally in contrast to findings of previous studies (Kafarov and Babanov, 1959; Rodriguez et al, 1961; Fernandes and Sharma, 1967) in liquid-liquid system. However, these investigations were conducted in turbulent conditions, whereas the present system operated under laminar to low-transitional regime. Drop breakage mechanisms in laminar conditions are quite different from those in turbulent conditions. Consequently under laminar conditions, it appears that the propeller provides greater breakage rates than the Rushton turbine.

Typically in applications dealing with high viscosity fluids, laminar flow impellers such as helical ribbons, screw and anchor impeller are used (Tatterson, 1991). These impellers provide high amount flow relative to shear (Oldshue, 1983). Although propellers are not classified as impeller suitable for laminar conditions, they are comparable more to laminar flow impellers than the Rushton turbine. As such one would expect the propeller to perform
better than the Rushton turbine given the laminar flow conditions prevailed in the present system. Conversion and drop size results clearly show that this is the case.

In heterogenous reactions, minimising coalescence is also desirable given that coalescence results in the formation of larger drops which in turn reduce the interfacial area available for reaction. Drop size measurement experiments show that the evolution of $d_{32}$ vary depending on the experimental conditions (Figures 4.1, 4.5, 4.6, 4.21, 4.23 and 4.24). Coalescence appeared to occur to a greater extent at lower dispersed phase volume fractions. Analysis also show that the relative rates of coalescence and breakage are functions of dispersion viscosity rather than the dispersed phase volume fraction itself. Therefore, in terms of promoting smaller drop sizes, it would be desirable to maintain a higher continuous phase viscosity.

Impeller speed has a significant impact on both conversion rates and drop sizes. Results produced by the Rushton with $\phi_i = 0.028$ suggests that higher impeller speeds produces greater conversion rates (Figure 5.2). For instance, values in Table 5.1 suggest that a three fold increase in speed (150 to 450) results in more than ten fold increase in conversion rates. Such comparison could not be made for the propeller due to a lack of conversion results. In terms of the impact of impeller speed on steady state $d_{32}$ (Figure 4.30), the Rushton was found to be more sensitive than the propeller. Coalescence rates (relative to breakage rate) were found to decrease with increasing impeller speed. Such information could be useful for reactor design and optimisation of PIBSA derivative emulsifier production process.
CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS
6.1 Conclusions

The purpose of the present investigation is to develop a greater understanding of a reactive liquid-liquid system used in the emulsion explosives industry. The main focus of the research is to examine the effect of design variables such as the impeller speed, the impeller type and dispersed phase volume fraction on drop size, conversion and ultimately interfacial area, a key component in liquid-liquid reactions. The main findings from the study are presented below.

Evolution of \( d_{32} \) produced four different trends in all drop size experiments. The likelihood of a certain trend to be present was found to depend on the impeller speed and the dispersed volume fraction and to a lesser extent, the impeller type. Trends are such that under certain experimental conditions the \( d_{32} \) values increases with time, whereas in other cases, \( d_{32} \) values decreases with time. There are also some instances, where \( d_{32} \) values increase initially with stirring time to reach a maximum value and then decrease to reach a steady state value. The transient viscosity results show that the continuous phase viscosity increases gradually for a period of time before reaching a constant value. Existence of different trends in \( d_{32} \) values has been attributed to the effect of viscosity change on the drop breakage and coalescence rates.

Similar to the evolution of \( d_{32} \), drop size distribution results produced four distinctive trends. In fact, the trends in \( d_{32} \) values provide an insight into DSD results and vice versa. For conditions where \( d_{32} \) decreases with time, the DSD narrows and shifts towards smaller drop sizes. When \( d_{32} \) increases, the DSD broadens and shifts towards larger drop sizes. Most distributions are log-normal with a peak at the low diameter side and a long tail on the large diameter side. However, at high impeller speeds and high dispersed volume fractions, the DSD tends towards being normal distribution.

Steady state \( d_{32} \) values were found to decrease with increasing impeller speed for all dispersed volume fractions and for both impeller types. A linear relationship of \( d_{32} \) versus \( N \) on log-log plot is found for all experimental conditions. This is consistent with the observations made by previous researchers and the values of the exponents are within the general range of results reported in those investigations. The exponents of the Rushton
turbine are -1.07, -1.31 and -1.19 for $\phi = 0.028$, 0.02 and 0.01 respectively. The propeller produced exponents of -0.47, -0.63 and -0.77 for $\phi = 0.01$, 0.02 and 0.028 respectively.

A linear relationship between dispersed phase volume fraction and steady state $d_{32}$ was found for all impeller speed and for both impeller types. However, the relationship between the two parameters ($\phi$ and $d_{32}$) was found to be inverse, which is totally opposite to the observations made in previous studies on liquid-liquid dispersions. Transient viscosity results show that $\mu_c$ increases with $\phi$. Given that $\phi$ and $\mu_c$ have opposing effects on $d_{32}$, the trends found suggests that the $\mu_c$ has the greater influence on the evolution of $d_{32}$ compared to $\phi$.

The steady state DSD was found to narrow and a shift towards smaller sizes with increasing impeller speed for all experimental conditions. Results also suggest that the steady state DSD narrows and shifts towards smaller sizes with increasing $\phi$ for all impeller speeds and for both impeller types.

The propeller was found to produce smaller values of steady state $d_{32}$ compared to Rushton turbine in the same operating conditions. The steady state DSD produced by the propeller was found to be narrower and on the smaller drop size side as compared to the distributions obtained with the Rushton turbine.

Attempts were made to fit the Steady state $d_{32}$ data obtained in the present investigation to existing correlations, namely those developed by Pacek et al (2001) and Kumar et al (1998). The latter correlation modified by incorporating the exponent of $N$ was found to successfully predict the drop size data obtained in the present investigation.

Sensitivity of the chemical analysis technique produces reactant concentrations only for limited number experimental conditions, for the Rushton turbine ($N \leq 450$, $\phi = 0.028$) and for the propeller ($N < 250$, $\phi = 0.028$). Results show that in all observed conditions the conversion occurs at an exponential rate. It was also found that an increase in impeller speed results in an increase in conversion rates. Furthermore, the propeller was found to produce greater conversion rates compared to the Rushton turbine in the same operating conditions. Chemical analysis indicated that the assumption of equimolar stoichiometry is valid for the present reaction. Using conversion data and assuming equimolar stoichiometry, time variant
dispersed phase volume fraction was obtained. Results show that the dispersed phase volume fraction decreases at an exponential rate for all impeller speeds and for both impeller types. The $\phi$ was found to decrease at a greater rate with increasing impeller speed and for the propeller compared to the Rushton turbine impeller.

Results show that the interfacial area decreases with time at all impeller speeds and for both impeller types. Given the opposite effects of the dispersed phase volume fraction and the Sauter mean drop diameter, it appears that the former has a dominant effect on the interfacial area. It was also found that the rate of decrease in the interfacial area increases with increasing impeller speed. This was despite the fact that higher impeller speeds produces smaller drop sizes. Furthermore, the results indicate that the interfacial area decreases at a greater rate for the propeller compared to the Rushton turbine impeller.

Correlation for the prediction of interfacial area for the present system was developed using a model developed for predicting transient dispersed phase volume fraction and the correlation used to predict steady state $d_{32}$ (equation 5.7). The model shows reasonable agreement with experimental result, but given the limited amount data available for model fitting, validity of this correlation is debatable.

### 6.2 Recommendations and Suggestions for Future Work

The present study examined the effect of the impeller speed, impeller type and the dispersed phase volume fraction on interfacial area. Result produced by the experiments conducted provides some useful information for PIBSA derivative emulsifier production, specifically reactor design.

Results certainly suggest that the propeller is the more suitable impeller for the production process compared to the Rushton turbine. This is based on fact that the propeller was able to generate smaller drop sizes, which in turn results in the greater interfacial area available for reaction and ultimately greater conversion rates compared to the Rushton turbine. The authors do not suggest nor recommend that the propeller should be used production process, but the results generated by the study implies that high flow/low shear impellers such as the propeller is considerably more efficient than low flow/high shear impeller such as the
Rushton turbine. Therefore, direction for future studies could be to conduct similar experiments using a several high flow/low shear impellers, namely impellers such as helical ribbons, screws, and anchor impellers.

Impeller speeds also has a significant impact on the drop size and interfacial area. As in most drop size studies increases in impeller speed generates smaller drop sizes. The evolution of $d_{32}$ and DSD results suggest, that increases in impeller speed not only increases breakage rates, but also reduces coalescence. The dispersed phase volume fraction has also appeared to have an impact on dynamics of the coalescence and breakage processes. Results show that the likelihood of coalescence occurring increases with decrease in dispersed phase volume fraction. This is attributed to change in viscosity rather than a direct effect of dispersed phase volume fraction. Rheological results show that decreases in viscosity results in the increase of coalescence, especially at low impeller speeds. Therefore more favourable drop size and interfacial area can be generated by maintaining the viscosity of the system at a reasonably high level.

The present study focuses on one of the components that constitute a rate equation for liquid-liquid reactive systems, namely interfacial area. Although a model to predict time variant interfacial area was developed, its validity is debatable. This is mainly due to limitation in the experimental techniques. Improvement in the experimental techniques would broaden the range of measurements that can be made and could give greater credence to the model. Therefore direction for future work could to driven towards achieving that.

Other components with that encompass the rate equation include the reaction rate constant, continuous phase and dispersed phase mass transfer coefficients and the distribution coefficient. Direction for future studies would be to examine and possibly develop models for each of these components. This will assist in the development of the reactor design equation for the emulsifier production process, which can ultimately lead to scale-up and optimisation.
REFERENCES


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Cherry, R. S., and Papoutsakis, E. T., 1986, Hydrodynamic effects on cells in agitated tissue culture reactors, Bioprocess Engineering, 1, 29-41.


Tanaka, M., 1985, Local droplet diameter variations in stirred tank, Canadian Journal of Chemical Engineering, 63, 723-727.


A.1. Rheological Properties of Materials

![Graph showing shear rate vs shear stress for pure PIBSA at 20°C.](image)

Figure A.1.1: Shear rate vs shear stress of pure PIBSA at 20°C.

![Graph showing viscosity vs temperature for mineral oil (PH833) at various temperatures.](image)

**Equation:**

\[ \mu = 0.1091e^{-0.0397T_m} \]

**R²:** 0.9935

Figure A.1.2: Viscosity of mineral oil (PH833) at various temperatures.
Figure A.1.3: Viscosity of the continuous phase (56% PIBSA/44% mineral oil) at various temperatures.

A.2 NMR Spectra
Figure A.2.1: $^1$H NMR spectrum of MEA.

Figure A.2.2: $^1$H NMR spectrum of mineral oil (PH 833).

Figure A.2.3: $^1$H NMR spectrum of PIBSA.
A.3 FTIR Spectra
Figure A.3.2: FTIR spectrum of mineral oil (PH 833).

Figure A.3.3: FTIR spectrum of PIBSA.
A.4 Error Analysis

Figure A.3.4: FTIR spectrum of the product mixture.

Figure A.4.1: Evolution of $d_{32}$ for the Rushton turbine impeller at 350 rpm, $\phi = 0.028$. 
Figure A.4.2: Transient conversion fraction of PIBSA for the Rushton turbine impeller at 150 rpm, $\phi = 0.028$.

Table A.4.1: Coefficient of determination, $R^2$ of DSD trendline and DSD data, Rushton turbine impeller.

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<th>Dispersed phase volume fraction</th>
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<td>R$^2$</td>
<td>Time (mins)</td>
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<td>Dispersed phase volume fraction</td>
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<td>-------</td>
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</tr>
<tr>
<td></td>
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<td>R²</td>
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Table A.4.2: Coefficient of determination, R² of DSD trendline and DSD data, propeller.
A.5: Flow regime

Figure A.5.1: Transient Reynolds number, $N_{Re}$ for $\phi = 0.028$ at various speeds, Rushton turbine impeller.

Figure A.5.2: Transient Reynolds number, $N_{Re}$ for $\phi = 0.02$ at various speeds, Rushton turbine impeller.
Figure A.5.3: Transient Reynolds number, $N_{Re}$ for $\phi = 0.01$ at various speeds Rushton turbine impeller.

Figure A.5.4: Transient Reynolds number, $N_{Re}$ for $\phi = 0.028$ at various speeds, Propeller.
Figure A.5.5: Transient Reynolds number, $N_{Re}$ for $\phi = 0.02$ at various speeds, Propeller.

Figure A.5.6: Transient Reynolds number, $N_{Re}$ for $\phi = 0.01$ at various speeds, Propeller.
A.6 Evolution of Drop Size Distribution

Figure A.6.1: Evolution of DSD for the Rushton turbine impeller at 200 rpm, $\phi = 0.028$.

Figure A.6.2: Evolution of DSD for the Rushton turbine impeller at 250 rpm, $\phi = 0.028$. 
Figure A.6.3: Evolution of DSD for the Rushton turbine impeller at 350 rpm, $\phi = 0.028$.

Figure A.6.4: Evolution of DSD for the Rushton turbine impeller at 600 rpm, $\phi = 0.028$. 
Figure A.6.5: Evolution of DSD for the Rushton turbine impeller at 150 rpm, $\phi = 0.02$.

Figure A.6.6: Evolution of DSD for the Rushton turbine impeller at 250 rpm, $\phi = 0.02$. 
Figure A.6.7: Evolution of DSD for the Rushton turbine impeller at 350 rpm, $\phi = 0.02$.

Figure A.6.8: Evolution of DSD for the Rushton turbine impeller at 450 rpm, $\phi = 0.02$. 
Figure A.6.9: Evolution of DSD for the Rushton turbine impeller at 250 rpm, $\phi = 0.01$.

Figure A.6.10: Evolution of DSD for the Rushton turbine impeller at 450 rpm, $\phi = 0.01$. 
Figure A.6.11: Evolution of DSD for the propeller at 250 rpm, $\phi = 0.028$.

Figure A.6.12: Evolution of DSD for the propeller at 350 rpm, $\phi = 0.028$. 
Figure A.6.13: Evolution of DSD for the propeller at 250 rpm, $\phi = 0.02$.

Figure A.6.14: Evolution of DSD for the propeller at 350 rpm, $\phi = 0.02$. 
Figure A.6.15: Evolution of DSD for the propeller at 250 rpm, $\phi = 0.01$.

Figure A.6.16: Evolution of DSD for the propeller at 350 rpm, $\phi = 0.01$. 
A.7 Steady State DSD

Figure A.7.1: Steady state DSD for the Rushton turbine impeller at various speeds, $\phi = 0.02$.

Figure A.7.2: Steady state DSD for the Rushton turbine impeller at various dispersed phase volume fractions, $N = 250$ rpm.
Figure A.7.3: Steady state DSD for the Rushton turbine impeller at various dispersed phase volume fractions, $N = 350$ rpm.

Figure A.7.4: Steady state DSD for the propeller at various impeller speeds, $\phi = 0.02$. 
Figure A.7.5: Steady state DSD for the propeller at various impeller speeds, $\phi = 0.01$.

Figure A.7.6: Steady state DSD for the propeller at various dispersed phase volume fractions, $N = 250$ rpm.
Figure A.7.7: Steady state DSD for the propeller at various dispersed phase volume fractions, \( N = 350 \) rpm.

A.8 Impeller Comparison

Figure A.8.1: Steady state Sauter mean drop diameter, \( d_{32} \) versus impeller speed for the propeller and Rushton turbine, \( \phi = 0.02 \).
Figure A.8.2: Steady state DSD for the propeller and the Rushton turbine impeller at 150 rpm, $\phi = 0.028$.

Figure A.8.3: Steady state DSD for the propeller and the Rushton turbine impeller at 350 rpm, $\phi = 0.028$. 
Figure A.8.4: Steady state DSD for the propeller and the Rushton turbine impeller at 150 rpm, $\phi = 0.02$.

Figure A.8.5: Steady state DSD for the propeller and the Rushton turbine impeller at 250 rpm, $\phi = 0.02$. 
Figure A.8.6: Steady state DSD for the propeller and the Rushton turbine impeller at 350 rpm, $\phi = 0.02$.

Figure A.8.7: Steady state DSD for the propeller and the Rushton turbine impeller at 150 rpm, $\phi = 0.01$. 
A.9 Drop Size Correlations

Figure A.8.8: Steady state DSD for the propeller and the Rushton turbine impeller at 250 rpm, $\phi = 0.01$.

Figure A.9.1: Comparison of experimental steady state $d_{32}$ produced by propeller and those calculated from equation 4.6.
Figure A.9.2: Comparison of experimental steady state $d_{32}$ produced by propeller and those calculated from modified equation 4.6.

A.10: Calculations of PIBSA Conversion

Molecular weight of MEA, $M_{MEA} = 61$ kg/kmol
Density of MEA, $\rho_{MEA} = 1014$ kg/m$^3$
Molecular weight of PIBSA, $M_{PIBSA} = 1085$ kg/kmol
Density of PIBSA, $\rho_{PIBSA} = 925$ kg/m$^3$
Initial volume fraction of PIBSA, $\phi_{PIBSA} = 0.545$
Initial volume fraction of MEA $\phi_{MEA} = 0.01, 0.02, 0.028$

Amount of PIBSA per volume of reactor

$$= \frac{\phi_{PIBSA} \times \rho_{PIBSA}}{M_{PIBSA}} = \frac{0.545 \times 925}{1085}$$
$$= 0.466 \text{ kmol/m}^3$$

If equimolar stoichiometry in the reaction is assumed, the amount MEA per volume of reactor required for full conversion of PIBSA, $n_{MEA} = 0.466$ kmol/m$^3$.

∴ Volume of MEA required for full conversion

$$= \frac{n_{MEA} \times M_{MEA}}{\rho_{MEA}} = \frac{0.466 \times 61}{1014}$$
$$= 0.028.$$

Amount of MEA per volume of reactor for $\phi_{MEA}$ of 0.01

$$= \frac{\phi_{MEA} \times \rho_{MEA}}{M_{MEA}} = \frac{0.01 \times 1014}{61}$$
$$= 0.166 \text{ kmol/m}^3$$
Assume equimolar reaction.
∴ Amount of PIBSA converted per volume of reactor = 0.166 kmol/m$^3$.

If total amount of PIBSA present in reactor = 0.466 kmol/m$^3$ (as per earlier calculations), the fraction of PIBSA converted with full conversion of MEA ($\phi_{MEA} = 0.01$) = \frac{0.166}{0.466} = 0.356 or 35.6% converted.

Similarly with $\phi_{MEA} = 0.02$, the fraction of PIBSA converted = 0.712 or 71.2% converted.