Identification of the nucleation locus in emulsion polymerization processes

Vineet, Shastry
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Identification Of The Nucleation Locus In Emulsion Polymerization Processes

by

Vineet Shastry

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
Department of Chemical Engineering
College of Engineering
University of South Florida

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LIST OF SYMBOLS

$A(\lambda)$  Absorption coefficient as function of wavelength
\[c\]  Concentration  in g/cc
CMC  Critical Micellar Solution
D  Diameter of the particles
\[D\]  Appreciable Decrease with the increase of the effect
dI  The change in the intensity of the light
Ex$_{total}$  Total extinction
Ex$_{small}$  Extinction of small particles
Ex$_{large}$  Extinction of large particles
f(D)  Particle Size Distribution
I  The intensity of the transmitted light
I$_0$  The intensity of the incident light
\[I\]  Appreciable Increase with the increase of the effect
k  Imaginary part of the refractive index
I  Path length
m  Complex Refractive Index
n  Real part of the refractive index
N$_p$  Number of particles
\[N\]  Not Appreciable

xv
\( N_{PE} \)  
Not Possible to Express

\( N_{surf\text{molecules}} \)  
Number of surfactant of molecules

\( N_{\text{smpla}} \)  
Number of particles of the size characteristics of the swollen or empty micelles for dispersing the estimated amount of oil

\( N_{\text{msmop}} \)  
Number of moles of surfactant required to stabilize small particle population

\( N_{\text{smop}} \)  
Total number of surfactant molecules required to stabilize the surface area of small particle population

\( P \)  
Principal value of the integral

\( \text{OD} \)  
Optical Density

\( Q_{\text{ext}} \)  
Extinction Coefficient

\( Q_{\text{absorbance}} \)  
Absorption efficiency

\( Q_{\text{scattering}} \)  
Scattering efficiency

\( R \)  
Radius of one droplet of the dispersed phase

\( S_{\text{stabreq}} \)  
The surface area of the small particle population

\( \text{S/O} \)  
Surfactant to Oil ratio

\( T \)  
Temperature

\( T_R \)  
Reduced temperature

\( T_c \)  
Critical temperature

\( V \)  
Volume of one droplet of the dispersed phase

\( V(T) \)  
Molar volume of decane hydrocarbon at temperature \( T \)
### Other Symbols

<table>
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<tr>
<td>$\tau_0$</td>
<td>Optical Density</td>
</tr>
<tr>
<td>$\lambda, \lambda_0$</td>
<td>Wavelength</td>
</tr>
<tr>
<td>$\lambda_i$</td>
<td>Initial Wavelength</td>
</tr>
<tr>
<td>$\lambda_f$</td>
<td>Final wavelength</td>
</tr>
<tr>
<td>$\varepsilon_{\text{extinction}}$</td>
<td>The extinction coefficient</td>
</tr>
<tr>
<td>$\Delta G_{\text{em}}$</td>
<td>Free Energy</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Interfacial Tension</td>
</tr>
<tr>
<td>$\mu_s$</td>
<td>Mean diameter of small particle population</td>
</tr>
<tr>
<td>$\sigma_s$</td>
<td>Standard Deviation of the small particle population</td>
</tr>
<tr>
<td>$%$</td>
<td>Weight percent</td>
</tr>
<tr>
<td>$\rho(T)$</td>
<td>Density of the hydrocarbon at temperature ‘T’</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Acentric factor</td>
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Identification of Nucleation Locus in Emulsion Polymerization Processes

Vineet Shastry

ABSTRACT

Particle Nucleation is the forcing function in the Emulsion Polymerization processes and it plays an important role in dictating the final properties of the latex produced. Identification of the main nucleation sites and characterizing them in terms of their size and composition is important for elucidating the mechanism of particle nucleation.

This research focuses on identifying the most likely nucleation locus in emulsion polymerization processes by characterizing the initial conditions of the reaction mixture. In order to achieve this objective, a methodology was devised, which used a non-reacting model emulsion system instead of the original emulsion. The model emulsion system selected has the same dispersion properties as that of the monomer emulsion system, but different optical properties. The model emulsion system enabled the study of the distribution of the emulsifier using Uv vis spectroscopy. This approach also eliminated the time constraint associated with sampling during a polymerization reaction. A quantitative deconvolution using the turbidity equation, was done on the transmission Uv vis spectra of the
emulsions. This enabled the characterization of the emulsions in terms of their particle size distribution, particle number and the composition of the droplet populations comprising them.

The studies conducted provide the experimental evidence for a previously unidentified nano-droplet population of size range 30 to 100nm in diameter. To further support this experimental evidence, calculations were performed to obtain the emulsifier distribution over the nano-droplet population. The calculations suggest the probability of existence of the nano-droplet population to be much higher than the probability of the existence of the swollen micelles.

The results, depending upon the emulsification conditions, indicate the presence of about 15 % to 80% of the dispersed phase in the nano-droplet population. The large interfacial area offered by the nano-droplet population due to their high particle numbers and high percentage of the dispersed oil phase in them, make them the most probable particle nucleation loci in emulsion polymerization processes.

Designed experiments were performed to experimentally observe the changes in the nano-droplet populations. The effects of the process variables, namely pH, surfactant concentration and temperature, on the size and compositional characteristics of the nano-droplet population were investigated. The results suggested that the surfactant to oil ratio was the dominating factor governing the size and the weight percent of the dispersed phase in the nano-droplet population.
CHAPTER 1: INTRODUCTION

1.1 Motivation

Particle nucleation is the forcing function in emulsion polymerization processes since it plays a significant role in the development of most of the properties of the final latex. The nucleation mechanism in emulsion polymerization is not fully understood and therefore it still remains an area of active research\(^1\). The main objective of this research effort is to identify the actual nucleation locus for the understanding of the nucleation mechanism in emulsion polymerization. This research proposes the use of optical techniques for the emulsion characterization in terms of its size and composition. This dissertation describes the model emulsion systems and the experiments based on them that provide relevant information for identifying the nucleation mechanism.

A brief description of the process is provided in this chapter in addition to giving a brief idea regarding the importance of Emulsion Polymerization processes. Explanation and reasoning for the main thrust of this research effort and the contributions as a result are described.
1.2 Significance of the Emulsion Polymerization Process

Emulsion Polymerization is a process of great industrial importance. It finds applications in the manufacture of a wide range of products such as paints, latex, adhesives, production of coatings and other synthetic materials. It also has applications in bio-separations through functionalization of the latex particles, and it offers great promise for the synthesis of nano-materials.

This process is a technologically and commercially important synthesis process. It grew rapidly in use as a result of the intense research into its application for producing synthetic alternatives to natural rubber latex during the Second World War. It is a basic process of a massive global industry that continues to expand due to the versatility of the reaction and greater realization of the ability to control the properties of the polymer latexes produced. Millions of tons of synthetic polymer latexes are prepared by this process for use as commodity polymers in a wide variety of applications, such as: synthetic rubber, high – impact polymers, latex foam, carpet backing, binders for non woven fabrics, adhesives, additives for construction materials such as Portland cement, mortar, concrete and sealants.

This industry has grown into a multi-million dollar industry today. From the reports on the International Institute for Synthetic Rubber Production almost 10.4 million metric tons of synthetic rubber latex was consumed world wide in the year 1998. Western Europe recorded the greatest consumption growth rate of 5.4% amounting to approximately 2.7 million metric tons. North America showed a growth rate 3.1% reaching nearly 3.1 million metric tons consumed in 1998. The global market in the year
1999 for the synthetic latex polymers was estimated to be about 13,500 million dry pounds\(^5\).

Worldwide Consumption of main polymer systems in the year 1999 as per the reports of Polymer Latex GMBH\(^6\) is as follows

**Table 1.1 Sale of the Emulsion Polymerization Products in the Year 1999**

<table>
<thead>
<tr>
<th>Polymerization Product</th>
<th>In Million tons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyvinyl chloride</td>
<td>24</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>12</td>
</tr>
<tr>
<td>Synthetic rubber</td>
<td>10</td>
</tr>
<tr>
<td>Synthetic latex</td>
<td>6.0</td>
</tr>
<tr>
<td>Other Emulsion products</td>
<td>4.6</td>
</tr>
</tbody>
</table>

As per the forecast of the market research conducted by the Paint and Research Association\(^7\) UK, the consumption of the environment friendly adhesive products until the year 2004 is expected to show an overall growth from 3 to 5% per year by volume. According to the market report published by the Freedonia\(^8\) group in October 2002, the emulsion polymer demand in the United States is expected to grow 2.8% annually to five billion pounds in 2006. Market value is expected to rise 4.4% per year to 4.3 billion dollars. Given the magnitude of these numbers, the impact of the Emulsion Polymer industry on the global economy can be appreciated.
1.3 A Brief Description of Emulsion Polymerization Process

The main advantage of the Emulsion Polymerization process is that it can be adjusted to tailor the properties of the product polymer and of the latex. A few important terms that are used throughout the dissertation for the description of the emulsion polymerization process are defined as below.

1.3.1 Important Definitions

1. Nano-droplets: Nano-droplets are the small droplets of the monomer with the size ranging form 30 nm to 100nm in diameter.

2. Time zero condition: Is the initial condition of the reaction mixture before the initiator is added to it (beginning of the reaction). Essentially at time zero, a liquid – liquid emulsion system with monomer as the dispersed oil phase in water (continuous phase) is present in the reactor.

3. Micelles: Aggregated molecules of surfactants of size range 1 nm to 3 nm in diameter.

4. Swollen Micelles: Micelles containing monomer; size range 5 to 10 nm in diameter.

5. Particle/ polymer particle: Swollen micelles with either dead or growing polymer chain; size range 20 to 80nm in diameter.

6. Monomer droplets: Droplets of monomer having size range one to a few microns.

7. Particle number: Total number of any particulate entity such as micelles, swollen micelles, particles, monomer droplets, nano-droplets etc.

8. Oligomeric radicals: The initiator radicals react with the dissolved monomer to form radicals which in turn react with the other dissolved monomer thus increasing
their chain length. Such radicals that have three to five monomer units (very short chain length) are called oligomeric radicals.

9. Forcing Function: Forcing function of an event is the factor primarily responsible for a particular process phenomenon.

1.3.2 Emulsion Polymerization Process

Emulsion polymerization is a free radical initiated chain polymerization in which a monomer, or a mixture of monomers, is polymerized in the presence of an aqueous solution of a surfactant to form a product known as latex. Latex is defined as a colloidal dispersion of polymer particles in aqueous medium. The main ingredients for conducting the emulsion polymerization reactions in addition to the monomer and water, include surfactants, initiators and sometimes chain transfer agents.

When the surfactant is added to water and the concentration of the surfactant is above the critical micellar concentration (CMC), the hydrophobic ends of some of the surfactant molecules come together to form micelles. These micelles are generally referred to as empty micelles as they only contain surfactant molecules. These micelles are about 5 nm$^1$ in diameter and their concentration as a function of the concentration of the surfactant above CMC is given by$^{1,9,10}$

$$\text{Number of micelles} = \frac{[S_{\text{added}}] - \frac{4 \* \pi \* r_s^2 \* N_s}{N_A \* a_s}}{n_{agg}} - [\text{CMC}]$$
where,

1. $[S_{\text{added}}]$ is the molar concentration of the surfactant added to the continuous phase.
2. $N_c$ is the particle number.
3. $[\text{CMC}]$ is the critical micellar concentration of the surfactant.
4. $N_A$ is the avogadro’s number.
5. $a_s$ is the area occupied by one surfactant molecule.
6. $n_{\text{agg}}$ is the mean aggregation number of the micelle.

The rest of the surfactant that does not form micelles but remains in dissolved form is termed free emulsifier. The monomer is then added to this aqueous solution of the surfactant. Some of the monomer enters the micelles. Such micelles are called swollen micelles. The average size of the monomer swollen micelles is 10nm$^9$. The rest of the monomer remains as monomer droplets. In other words, the otherwise immiscible oil phase (in this case monomer) is dispersed into the water phase. An emulsion of oil in water is thus obtained. Some of the emulsifier surrounds the monomer droplets to maintain the stability of the emulsion.

The emulsion polymerization reaction is initiated by the addition of the initiator. The initiation mechanism or the mechanism of primary free radical formation is helpful in addressing the number of free oligomeric radicals that will be formed. The primary free radicals react with the dissolved monomer in the aqueous phase to form the oligomer radicals which play an important role in nucleation as per the existing (micellar and homogeneous coagulative and droplet) nucleation theories$^{11}$. 

6
Emulsion Polymerization reactions can be divided into stage I, stage II and stage III. The stage I of the emulsion polymerization reaction is characterized by the disappearance of micelles and formation of particles (or particle nucleation). The stage II is characterized by the growth of the particles and the presence of monomer droplets, while the stage III is characterized by the disappearance of the monomer droplets.

The three main proposed and widely accepted (to different degrees) particle nucleation mechanisms are:
1. Micellar nucleation
2. Homogeneous and coagulative nucleation
3. Droplet Nucleation

An elaborate discussion on the merits and limitations of the proposed nucleation theories is presented in Chapter 2. Particles are primarily formed in the stage I as per the dominant nucleation mechanism. The particles grow in size as the reaction progresses inside them. The monomer droplets serve as the supply reservoirs of the monomer to the particles in which the reaction is taking place. The emulsifier gets redistributed for maintaining the stability of the latex mixture as the reaction proceeds, since the interfacial area between the particulate entities changes. Due to the growth in the particle size and the change in the particle number, the interfacial area between the particles and the continuous phase changes continuously for the stage I of the reaction. The number of particles remain constant but the particles continue to grow in size as the reaction progresses to the stage II. This causes a change in the interfacial area between the
dispersed phase and the continuous phase even during the second stage of the reaction. The monomer droplets present in the emulsion provide the growing particles with monomer. During the second stage, the entry of another radical inside the polymer particle could either terminate a growing chain or could help in the propagation of an already existing dead polymer chain inside the particle in case branching or chain-transfer reactions are present. Each particle acts as a bulk reactor where the polymerization reactions occur. The second stage of the emulsion polymerization reaction is thus characterized by the growth of the polymer particles and decreasing size of the monomer droplets.

The third stage in the emulsion polymerization reaction is characterized by the disappearance of the monomer droplets. As more monomer is used, the monomer droplets providing monomer to the growing polymer particles gradually decrease in size and finally disappear. This marks the beginning of the last stage of the reaction. The reaction inside the polymer particles continues until it finally ends due to the lack of any further availability of the monomer. Figure 1 is a representation of the reaction mixture typically present inside the reactor.
1.4 Significance of the Research

Proper understanding of particle nucleation or particle formation is important since it governs:\n
1. The number of particles formed in an unseeded emulsion polymerization reaction
2. Particle size and hence the particle size distribution
3. The generation of particles depends upon the nucleation conditions.
   It is therefore necessary to determine the operating conditions required to avoid or to generate new crop of particles.
4. Rate of emulsion polymerization, and therefore the reaction dynamics, is proportional to particle number.
1.5 Outline of the Dissertation

Different nucleation theories proposed to date, are discussed along with their merits and limitations in the chapter on literature review of this dissertation. In this chapter are also described, the initial efforts made at USF for understanding the nucleation mechanism in emulsion polymerization. A brief history of the research, inclusive of the experimental work and development of the data analysis techniques is presented.

In the Chapter 3 is delineated the problem statement. This chapter focuses and justifies the strategic approach followed in addressing the problem of identifying the nucleation locus in emulsion polymerization. The arguments presented to justify the approach are supported by the results obtained via computer simulations. This chapter presents the main hypothesis of this work and discusses its relevance in understanding the nucleation mechanism.

In the Chapter 4, is outlined the experimental work undertaken in this research effort. The experiments with the model systems are explained and justified.

Chapter 5 is focused on the results of initial condition experiments performed with the model system. Discussion on the significance of the results and its implications pertaining to the understanding of the initial conditions for an emulsion polymerization reaction is presented.
In the Chapter 6 the conclusions of this research and makes recommendations for future work are summarized.

1.6 Contributions

Some of the contributions of this research effort are:

1.6.1 Identification of the Main Locus for Nucleation in Emulsion Polymerization

There exists a controversy pertaining to the locus of nucleation. Theories that are accepted to different degrees, propose different particulate entities as the reaction locus for the reaction to occur. Micellar nucleation theory proposes the monomer swollen micelles as the main nucleation locus\(^1,2\) while the homogeneous nucleation considers the precipitated oligomeric radicals as the main nucleation locus. The homogeneous and coagulative nucleation mechanism considers the precursor particles as the main nucleation locus\(^1,2\) while the droplet nucleation theory attributes the main reaction locus entity to the monomer droplets. Thus, identification of the main nucleation loci in emulsion polymerization reactions constitutes a contribution from this research effort.

1.6.2 Characterizing the Emulsifier Distribution as a Function of Initial Emulsification Conditions in an Emulsion Polymerization Reaction

The emulsifier concentration has a great influence over the size and compositional characteristics of the dispersed phase along with the other initial emulsification conditions such as temperature, rate of shear, pH of the suspending medium. Emulsifier distribution as a function of the initial conditions specified above for a stable emulsion, determines the size and the compositional characteristics of the actual nucleation locus.
1.6.3 Implementation of Spectroscopic Techniques to Identify the Nucleation Mechanism

A rapid and minimally–invasive measurement technique enabling continuous characterization of the particulate system present inside the reactor with minimal sample preparation is implemented. This technique can thus serve as an important tool for the continuous monitoring of the emulsion polymerization process in the industry.

1.6.4 Emulsion Characterization

Characterization of the dispersed phase in terms of its size and the compositional characteristics as a function of emulsification conditions is of fundamental importance to understand the emulsification process. Implementing the spectroscopic techniques enable the comprehensive characterization of the dispersed phase.
CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

A number of theories have been proposed to explain the nucleation mechanism in emulsion polymerization in the past. The particle nucleation phenomenon continues to be an area of active debate\textsuperscript{1}. Various researchers have proposed different theories based upon their experimental evidences and mathematical modeling for explaining the nucleation mechanism in emulsion polymerization. The objective of this chapter is to highlight the controversy in the proposed main nucleation locus postulated by different theories put forth to date.

The controversy on the main nucleation locus can be attributed to the limitations of the existing experimental capabilities available for the researchers for completely characterizing the reaction mixture present inside the reactor at early times of the reaction. This chapter provides a brief backdrop of the theories that have been proposed for the nucleation mechanism and the main nucleation locus suggested by each of them. A discussion on the merits and limitations of each of the proposed theories is also presented. The efforts undertaken over a period of years to identify the nucleation mechanism at the University of South Florida, by the research group of the Polymer Synthesis and Characterization Laboratory are briefly described.
2.2 Proposed Nucleation Mechanisms and their Limitations

Harkins’ mechanism as explained by Mohammed S. El-Aasser\textsuperscript{2}, states that the major source of particle nucleation is the monomer swollen surfactant micelles. According to Harkins, radicals generated in the aqueous phase enter the monomer-swollen micelles and initiate polymerization to form monomer swollen polymer particle nuclei. The monomer swollen particles grow by polymerization of monomer supplied to them by the monomer droplets by diffusion through the aqueous phase. The particle nucleation stage ends with the disappearance of the micelles. The major locus of polymerization was postulated to be the monomer swollen micelles. The above mentioned nucleation mechanism is called the micellar nucleation. The monomer swollen micelles supposed to be the main reaction sites (reaction loci) as per the micellar nucleation theory are around 5 to 10 nm in diameter. The micellar nucleation mechanism generally results because of low monomer solubility.

The quantitative development of the Harkins’ theory of emulsion polymerization kinetics was published by Smith and Ewart in 1948 with a first attempt at verification by Smith\textsuperscript{2}. Smith and Ewart’s equations\textsuperscript{12} predicted the rate of polymerization being directly proportional to the number of particles. The number of particles were predicted to be proportional to the $2/5^{th}$ power of initiator concentration and $3/5^{th}$ power of surfactant concentration. The predicted orders of initiator concentration and surfactant concentration were verified experimentally for styrene\textsuperscript{12}. The congruence of the order of concentration
of the initiator and the surfactant predicted by the Smith Ewart’s theory with the experimental observation was widely quoted as evidence for the micellar theory for nucleation. Gilbert, El Aaser cite Roe in pointing out, that the same two exponents can be predicted by a homogeneous – nucleation mechanism or any other model for nucleation mechanism considering complete surface coverage by surfactant as one of the governing events for the cessation of particle formation. The equations derived by Roe, which are identical to Smith –Ewart equations without considering micellar entry are reported by El Aaser. According to Roe (as cited by El Aaser), particle generation occurs at each interaction between dissolved free radical and dissolved monomer molecule and continues until the surfactant is depleted to a level not sufficient to stabilize new particles through adsorption. Roe demonstrated that though the micelles are an important source for particle formation, they were not necessary.

Alexander Dunn reproduces these derivations of Smith and Ewart’s equations for the rate of polymerization for Case 2 scenario. Case2 scenario is observed when the number of radicals per particle is equal to 0.5. When the Case 2 kinetics apply, the rate of polymerization of a particle is constant, independent of particle size or rate of the entry of the radicals if the concentration of the monomer inside the particles is constant.

Alexander Dunn further states that the effect of the ionic strength of the aqueous phase was not considered. Other implicit assumptions namely
1. “No difference in the area occupied by an emulsifier at the polymer-water interface and at the air-water interface.”

2. “Independence of the area occupied by an emulsifier to the presence of the monomer or other swelling agents in the particles were subsequently found to be incorrect.”

Gardon\textsuperscript{14} showed that the validity of the Smith and Ewart’s theory is confined to specifiable intervals of conversion, to a certain range of monomer/water ratio, and to the surfactant concentrations whose upper and lower limits are given. Gardon\textsuperscript{14} explicitly states the important assumptions underlying the Smith and Ewart theory namely, monomer swollen latex particles being the main locus of reaction, initiation of polymeric chains by the entry of the radicals from the water phase into the particles, instantaneous chain termination and nucleation by radical absorption by the particles containing the growing chain or the monomer swollen micelles. Gardon\textsuperscript{14} calculated the conversion at which the particle nucleation is complete along the predictions for particle size distributions. Based on the assumptions of the Smith Ewart theory, the relationship between the final number of particles formed as a function of the rate of radical production per cubic centimeter of water, fraction of monomer in the particles and bulk rate of polymerization were derived.

Gilbert\textsuperscript{1} and Dunn\textsuperscript{12} refer to Fitch and Gardon to point out, that quite a wide range of exponents of the surfactant concentration and initiator concentration proportional to
the number of particles at the end of the reaction is actually observed and also that the experimental data do not always obey a simple power law when plotted accurately.

El Aaser\textsuperscript{3}, cites the investigation of vinyl chloride emulsion polymerization and vinyl acetate emulsion polymerization by Jacobi and Priest respectively, as the first to report on homogeneous nucleation. The precipitated oligomeric radicals form the spherical particles, adsorb surfactant to form primary particles thus becoming the main loci of nucleation. Hansen, Ugelstad, Fitch and Tsai put forward the theory of homogeneous nucleation commonly referred to as the HUFT theory as reported by Gilbert\textsuperscript{1}. Since the coagulation events are included in the extension of the HUFT theory, it is also referred to as the homogeneous and coagulative nucleation theory. Gilbert\textsuperscript{1} gives a detailed illustration of the sequence of events for the HUFT theory. Works of Napper and Gilbert\textsuperscript{1,2,15} at University of New South Wales, Sydney Australia, propose that particle nucleation involves at least two mechanistic steps as opposed to the single step process for micellar nucleation or homogeneous nucleation. The first step is the formation of the “precursor particles” due to homogeneous nucleation and the second step is the formation of the mature particles by the aggregation of the precursor particles. Gilbert refers to the work of Feeney\textsuperscript{1} et al to show that carrying out emulsion polymerization in a polyacrylamide gel can isolate the precursor particles. By doing so, it can be ensured that the small particles could not coagulate. Particles of radius 5nm measured by small angle neutron studies were found to be isolated by these methods and could be stored indefinitely. Compositional information of the particles could thus be
obtained. However, the quantitative information on the number of precursor particles, which is critical in deciding the most likely nucleation locus, cannot be obtained using this method.

In quantifying the homogeneous nucleation for mathematical formulation purposes, the competition between entry (capture) of newly formed radicals and the radicals that form the precursor particles is taken into account along with the knowledge of the aqueous phase chemistry in emulsion polymerization.

Nucleation below the CMC of the surfactant is better explained by HUFT theory. Gilbert argues that homogeneous and coagulative nucleation is still the dominant mechanism for the emulsion polymerization carried out at surfactant concentration above CMC.

Gilbert and Napper briefly summarize the principal mechanism that may be operative in particle nucleation in a given system. They inferred that it is impossible to use the polymerization rate data alone to make any mechanistic deductions concerning nucleation. The polymerization rate data may be used in conjunction with other observable experimental data to provide mechanistic information on particle formation. They consider the experimental observations so as to obtain information on nucleation. The observations considered are polymerization rate, particle formation rate, particle size distribution for the case study of polymerization of styrene.
The objective of the measurement of the appropriate quantities of the small particles was not attainable by the experimental techniques available to Gilbert and Napper\textsuperscript{4}. Dependence of the particle number on the concentration of the surfactant and initiator and the data on the change in the number of particles as a function of time in conjunction with other measurements can provide very useful information on the mechanism of particle formation.

Particle size distribution (PSD) data was used to provide means of refuting mechanistic suppositions. Apart from the mean and standard deviation of the full particle size distribution, Gilbert and Napper\textsuperscript{1,2} suggest that the sign of the skewness of the particle size distribution towards the smaller sizes is indicative of the dominant mechanism. Gilbert and Napper\textsuperscript{1,16} have reported the PSD at times during the inception of the second stage to gather the mechanistic information of the nucleation process that essentially and predominantly occurs during the first stage of the reaction.

The nucleation mechanism theory that could explain the experimentally observed positive skewness of the particle size distribution during the inception of the second stage is the approach proposed by Gilbert for identifying nucleation mechanism.

Gilbert\textsuperscript{1,13,15} cites the positive skewness of the particle size distribution at the end of the nucleation stage, plotted as a function of particle volume as the evidence for the theory of homogeneous and coagulative nucleation. The positive skewness at the end of
the nucleation stage will indicate the high probability of the existence of smaller particles at the end of the nucleation stage. Positive skewness of the distribution indicates that the rate of nucleation is an increasing function of time. The high probability of most of the particles being small at the end of the nucleation stage indicates that most of the particles were formed during the later times of the nucleation period. Had the particles formed earlier, they would have grown as the reaction progressed throughout the first stage. Thus the probability of obtaining larger particles at the end of the nucleation stage would be higher. A negatively skewed distribution would thus be obtained.

Gilbert’s two step mechanism of homogeneous and coagulative nucleation is the only theory that predicts nucleation rate as an increasing function of time. The particle size distributions for the particle generation by micellar entry or simple homogeneous nucleation\(^3\) is characterized by negative skewness which in turn is indicative of nucleation rate as a decreasing function of time. This implies that most of the particles are formed in the later times of the 1\(^{st}\) stage of the reaction. Micellar theory predicts a decrease in the rate of nucleation suggesting that most of the particles are formed during the early times in the 1\(^{st}\) stage of the reaction. Similarly the single step homogeneous nucleation mechanism too predicts nucleation rate as the decreasing function of time. According to Gilbert and Napper\(^{16}\), the calculated and observed particle size distribution of the system and the calculated change in the number of particles as a function of time refute single step micellar and homogeneous nucleation mechanism for particle formation of styrene system under consideration. As per them, the behavior of nucleation rate as
increasing function of time can be explained by sequential coagulation only. The positive skewness of the particle size distribution expressed in terms of unswollen volume is indicative of homogeneous nucleation followed by coagulative nucleation, rather than a single step micellar or homogeneous nucleation.

PJ Feeney\textsuperscript{15} presents a detailed theory for nucleation kinetics in emulsion polymerization systems based on the coagulation of precursor particles. The coagulative theory presented combines extended Muller – Smoluchowski coagulation kinetics with DLVO theory\textsuperscript{15}. Feeney\textsuperscript{15} provides the mathematical expressions for the time evolution of the nucleation rate, particle number and particle size distribution. With physically reasonable values for the parameters for the coagulation kinetics, Feeney obtained agreement with the early time evolution of PSD which is essentially sensitive to the assumptions pertaining to the nucleation mechanisms since different nucleation mechanisms having different mechanistics would predict different shapes of the PSDs. Feeney also obtained excellent agreement with the data on the dependence of particle number on surfactant and initiator concentrations. Feeney\textsuperscript{15} observed positive skewness of the particle size distribution for different surfactants, which according to him is a conformation of coagulative nucleation theory for nucleation mechanism.

The observation of positively skewed distribution of the particles at the inception of the second stage is thus cited as the primary experimental evidence for supporting the homogeneous and the coagulative nucleation mechanism as the actual mechanism of
nucleation in emulsion polymerization\textsuperscript{1,2}. The primary precursor particles and their sizes are typically around 10 to 15 nm in diameter\textsuperscript{3} are supposed to be the main nucleation sites by this nucleation mechanism theory.

Jorge Herrera Ordonez and Roberto Olayo\textsuperscript{9,10,17} in their recent works question the evidence put forth by Gilbert. In doing so they cite Morrison in pointing out that the differences in the growing rates of different size particles can cause a positively skewed distribution of the particles at the end of the first stage. According to Morrison, as reported by Ordonez and Olayo\textsuperscript{9,10}, neither the homogeneous nucleation nor the homogeneous and coagulative nucleation is able to produce the experimentally observed concentration of the polymer particles in emulsion polymerization above the CMC. Furthermore Herrera-Ordonez\textsuperscript{9,10} states that the extension of the Derjaguin -Landau-Verwey -Overbeek (DLVO) theory to model the behavior of the very small latex particle like those in interval I can be debated. Herrera-Ordonez\textsuperscript{7} refers to Hansen in doubting the possibility of the completely covered particles being sufficiently unstable to coagulate. Herrera-Ordonez\textsuperscript{10} in presenting his arguments, refers to the work undertaken by Giannetti to argue that the homogeneous and coagulative nucleation is not the only mechanism due to which the particle formation above the critical micellar concentration takes place. Herrera- Ordonez\textsuperscript{7,8} refer to the modeling of particle size distribution done by Giannetti by using two methods namely the zero – one approach as originally formulated by Gilbert and Napper and the generating function approach. His results were contrary to the results of Gilbert and Napper, since neither model was able to fit for increasing nucleation
rates$^{9,10}$. Instead these data fitted nicely when a prevailing decreasing rate of the formation of mature particles was assumed. Giannetti argued that most of the mechanistic information inferred from early – time particle size distribution obtained from the experiments performed by Lichti$^{9,10}$ et al is lost because of the stochastic broadening of the PSD that occurs after nucleation stops. This reasoning was based on the observation, that the nucleation time was much smaller than the sampling time needed to obtain the experimental particle size distribution data.

Herrera-Ordonez and Roberto Olayo$^9$ propose a detailed mathematical model for the kinetics of styrene emulsion polymerization. The model predicts that micellar nucleation dominates over homogeneous nucleation and that the evolution of the nucleation rate reaches a maximum, where desorbed radicals have an important contribution. The results of this model developed were discussed and compared against the experimental data$^{9,10}$. The theoretical results, which were obtained without the coagulation of the particles being taken into account were congruent with the experimental data of the evolution of the styrene monomer conversion and the rate of polymerization. They concluded that if coagulative nucleation takes place above the critical micellar concentration, it is not significant$^{9,10}$. They further examine the same mathematical model for describing the emulsion polymerization of methyl methacrylate monomer above the CMC of the surfactant$^{17}$. On the basis of the model results they argued that the observed bimodal PSD and the rate polymerization PSD, need not necessarily be ascribed to the secondary nucleation. According to them, the predicted
PSDs in the early time during the first stages of the reaction can also be caused due to the differences in the growing rate of different size particles as predicted for styrene emulsion polymerization\(^9,10\) apart from sequential coagulation as advocated by Gilbert\(^7\).

The monomer concentration in the particles and the micelles during the first stage of the reaction show considerable size dependence if there are very small (< 10nm)\(^1\). The values can be considerably smaller than the normal values predicted by Morton’s equation\(^1\). Ordonez and Olayo\(^9,10\) did not consider the above mentioned size dependent compositional characteristic of the particles while developing their model for identifying the dominant nucleation mechanism.

C. S. Chern and C.H. Lin\(^18\) used a water insoluble dye as a probe to study particle nucleation in semi-batch emulsions polymerization of methyl methacrylate. From the results obtained from their experimental efforts that involved the determination of the quantity of a water insoluble dye incorporated into the latex particles, Chern and Lin\(^18\) conclude that homogeneous nucleation plays a key role in the particle formation period when the surfactant concentration is below CMC. When the surfactant concentration is above the CMC, mixed modes of particle nucleation (micellar and homogeneous nucleation) are operative in the polymerization system.

The hypothesis on droplet nucleation (monomer droplets being the most likely reaction loci) was dismissed by Mohammed S and El Aasser\(^3\) on the grounds of the low
availability of the interfacial area thereby decreasing its likeliness of occurring in conventional emulsion polymerization. However, the droplet nucleation was accepted to be the primary nucleation mechanism in mini-emulsion polymerization. Though it was initially expected that all the droplets would successfully compete for radicals thereby becoming polymer particles, it was found that only a relatively small fraction (less than 20%) succeeded in converting themselves into polymer particles by this process. The mechanism of disappearance of droplets in miniemulsion polymerization other than by becoming polymer particles still remains an unanswered question. Collision between droplets and existing particles and diffusion are the two main possibilities that have been widely cited.

Increase in the interfacial area of a given particulate entity and the continuous phase, increases the probability of the oligomeric radicals coming in contact with that particular particulate entity. The interfacial area made available by a particular entity would increase the chances of that particulate species to become the main locus for nucleation. Since the size of the monomer droplets is much larger as compared to the other particulate entities (like the swollen micelles) the surface area offered by them is considerably lesser than the smaller particulate species thereby decreasing their likeliness of being the main locus of particle nucleation.

From the literature cited in this section we can appreciate the fact that there remains a great deal of controversy regarding the main locus of nucleation and its
composition. The controversy on the most likely nucleation locus is expected to seriously hamper the elucidation of nucleation mechanism in emulsion polymerization process. The efforts undertaken at USF for addressing the nucleation mechanism are discussed in the next section.

2.3 Direction of Ongoing Research at USF

The controversy pertaining to the main nucleation loci can be attributed to the unavailability of the experimental capabilities that allow the complete characterization of the particle (droplet) populations comprising the emulsion mixture present inside the reactor at the inception of the polymerization reaction. Complete characterization of the reaction mixture at the inception of the reaction (also referred as time \( t = \) zero condition in this dissertation) involves obtaining quantitative information on the populations of the in terms of particle number and their composition\(^1\) and qualitative information regarding the true size distribution of each of them, simultaneously. This information is the key for refuting, accepting or proposing the mechanisms for nucleation\(^2\). It was for these reasons that a sensor array was developed and implemented as a part of our ongoing research work to enable the monitoring of the critical parameters for emulsion polymerization reaction continuously, simultaneously and in real time throughout the reaction. Relevant information required for identifying the most likely nucleation locus was intended to be obtained by extrapolating the data on critical parameters to time zero.
The critical parameters of the reaction mixture monitored throughout the reaction using this sensor array were:

1. Composition of the particles

2. Free emulsifier concentration and

3. Size distribution of the particle and droplet population/s

Online densitometer was employed in obtaining the online estimate of the conversion of the reaction mixture. The inline estimate of the interfacial tension was obtained by implementing the inline surface tensiometer. Jaime Vara\textsuperscript{21} has described in great detail the implementation of the densitometer and the surface tensiometer. The sensor array developed at our laboratory incorporated the spectroscopic measurements for characterizing the latex mixture throughout the reaction apart from the densitometer and interfacial tension measurements. This sensor array is described in detail in Appendix H.

A discussion supporting the choice of the spectroscopic techniques over other available techniques for investigating the number and size distribution characteristics of the particle populations comprising the emulsion / latex present inside the reactor is presented henceforth.

Giannetti\textsuperscript{10} underscores the need to have fast and reliable measurements that would provide information on the actual particle size distribution data of the particle populations present in the latex for understanding the nucleation mechanism. According to Gilbert\textsuperscript{1}, the complex nature of the process such as number of phases present etc, forces a need to introduce parameters that cannot be determined by prior information.
To obtain information on particle size distribution a number of techniques have been used by a number of researchers. Angular light scattering, small angle neutron scattering and transmission electron microscopy are the most widely used ones. These techniques are unable to provide an estimate of particle number and hence cannot provide adequate information required for investigation of nucleation mechanism in emulsion polymerization. Information on particle number of a particular particulate population is very pertinent in deciding the reaction locus, since the probability of a particular particle population becoming the main reaction loci increases with its increasing particle number. Microscopic techniques (including Transmission Electron Microscopy) are inadequate in characterizing liquid – liquid systems due to instability in the “fix” stage. Boundaries for the particles of size range below 10 nm appear fuzzy due to inadequate differences between the refractive index. This makes the results of the particles with size range below 10nm unreliable.1

The above discussion underscores a need of an experimental technique that can completely characterize the reaction mixture present in the reactor throughout the reaction, quickly, continuously and in real time throughout the reaction. The development of techniques for characterizing the reaction latex mixture from its online transmission Uv vis spectrum provide the qualitative and quantitative information necessary to identify the most likely nucleation locus.

Garcia Rubio22 has demonstrated the change in the shape of the transmission Uv vis spectrum as a function of particle size for well-characterized polystyrene standards.
C. Bacon\textsuperscript{23} and E Stiemle\textsuperscript{24} explored the potential of these spectroscopic techniques to a great degree by developing prototypes for obtaining multi angle multi wavelength measurements to obtain information on size distribution characteristics of particle populations. Andres Cardenas\textsuperscript{25} explored the limits and applicability of this measurement technique including reflectance spectroscopy. S. Fisher\textsuperscript{26} and S. Thennadi\textsuperscript{27} modeled the colloidal systems from the perspective of particle-particle interactions. From the Uv vis transmission spectrum of the reaction mixture, information on the number of particulate populations, number of particles contained in each population and the composition of the particles of each population can be obtained. J. Mehta\textsuperscript{28} S. Marathe\textsuperscript{29}. D. Imeokparia\textsuperscript{30}, S. Shetty\textsuperscript{31}, P. Vinnik\textsuperscript{32} obtained information on the initiation efficiency using labeled initiators to measure the rate of radical entry per particle. Obtaining the transmission Uv vis spectrum of the particulate mixture inside the reactor continuously and in real time was made possible by the development of the continuous sampling and parallel dilution system developed and patented by University of South Florida, Tampa\textsuperscript{33}. Characterization of the particulate systems on the basis of their particle number, particle size distribution, chemical composition from their transmission Uv vis spectrum was made possible by the algorithms which were based on Mie scattering theory developed by Dr Luis H Garcia Rubio\textsuperscript{34,35}. Paul Sacoto\textsuperscript{33} gives the information in detail on the development and the implementation of the continuous sampling and parallel dilution system.
Maria Celis de Arce\textsuperscript{36} successfully employed the spectroscopy technique for the measurement of the droplet size distribution as a function of the oil phase concentration and emulsifier concentration. She concluded that the results obtained from the light scattering interpretation models are applicable in the qualitative analysis of the liquid-liquid emulsions. Maria Celis suggested that, from the single scattering models it could be safely inferred that sample integrity can be preserved even after successive dilutions\textsuperscript{36}. This inference thus enables the use Uv vis spectroscopy as a tool for characterizing the reaction mixture to address the problem of nucleation mechanism in emulsion polymerization.
CHAPTER 3: PROBLEM DEFINITION

3.1 Introduction

The issues associated with the main theories put forth until date for explaining the nucleation mechanism in emulsion polymerization have been discussed in the literature review section of this dissertation. In the light of these issues, the importance of identifying the most likely nucleation site to elucidate the nucleation mechanism has been highlighted. This chapter focuses on the preliminary studies for formulating the hypothesis for identifying the most likely nucleation locus and on the direction for the necessary experimental work. The relevance of the proposed hypotheses for identifying the nucleation mechanism is discussed.

3.2 Approach

Elucidating the nucleation mechanism in emulsion polymerization is the long-term goal of this research effort. In order to achieve this objective, this research focuses on exploring the “time zero” condition of the emulsion polymerization reaction for identifying the most likely nucleation. The limitations of the experimental techniques available to the researchers for reaction mixture characterization at time zero have been described briefly in the earlier chapter. Implementation of the UV Vis spectroscopic techniques in order to overcome the limitations of the existing experimental methods for the complete characterization of the reaction mixture has also been discussed.
Characterizing the reaction mixture throughout the reaction in terms of the critical parameters and extrapolating the interval I rate data to time zero for investigating the time zero condition was the approach undertaken by the researchers to date. However, the dynamics of the reaction and the sampling issues presented considerable difficulties. In order to overcome this difficulty, this research takes the approach of characterizing the emulsion present inside the reactor at time zero, using a non-reacting “model emulsion system”.

A model emulsion system is an emulsion system comprised of constituents displaying similar dispersion behavior of the monomer emulsion system under similar emulsification conditions but having different optical properties.

The rationale for taking the approach for performing the experiments with the model emulsion system is provided in the detail in the experimental section of this dissertation (Chapter 4) along with the details of the system. The key issues necessary to understand the nucleation mechanism namely,

1. Plausible nucleation loci
2. Emulsifier distribution as a function of emulsification conditions
3. Size dependent compositional characteristics of the plausible nucleation locus
were addressed with the above mentioned model system and characterization techniques.
3.2.1 Preliminary Studies

Prior to performing the experiments with the model system mentioned above, simulation studies relating the size distribution and compositional characteristics of the styrene latex mixture to the characteristics of its transmission Uv vis spectra were undertaken. The Uv vis spectrum for the styrene latex with known optical properties, but different size distribution characteristics were simulated and compared with the experimentally obtained spectra. This was done to explore the possibility of the number of droplet populations likely to be present and to determine their characteristics. The details pertaining to these simulations are outlined in 3.2.2. Simulations were performed with the help of the algorithms developed in-house\textsuperscript{34,35}. The inferences drawn from the results from the simulation studies lead to the formulation of the main hypotheses in this research effort.

3.2.2 Algorithms Implemented

The simulation programs\textsuperscript{34,35} enabled the prediction the spectra on the basis of the latex properties. These algorithms\textsuperscript{34,35} incorporated the turbidity equation (equation 3.1) to calculate the transmission spectral features of latex with known optical properties. The turbidity equation relating the transmission spectrum of each of the particulate population to its particle size distribution, composition and particle number is based on the Mie scattering theory.
The turbidity equation is given by\(^{37}\),

\[
\tau_0(\lambda_0) = N_p \cdot I \left( \frac{\pi}{4} \right) \int Q_{ext}(m(\lambda_0), D) \cdot D^2 \cdot f(D) dD
\]

(3.1)

where

1. \(\tau_0(\lambda_0)\) is the optical density as a function of wavelength \(\lambda_0\)
2. \(N_p\) is the number of particles
3. \(I\) is the path length
4. \(m(\lambda_0)\), is the complex refractive index as a function of wavelength \(\lambda_0\)

\[m(\lambda_0)\text{ is generally expressed as }^{37} \frac{n(\lambda_0)}{n_0(\lambda_0)} + i\frac{k(\lambda_0)}{n_0(\lambda_0)}\]

where \(n(\lambda_0)\) is the real part of the refractive index and \(k(\lambda_0)\) is the imaginary part of the refractive index
5. \(Q_{ext}\) is the extinction coefficient (function of the complex refractive index and the size of the particles)
6. \(D\) is the diameter of the particles and \(f(D)\) is the particle size distribution of the particles.

From the turbidity equation, it can be inferred that the shape of the simulated spectrum is sensitive to the particle size distribution of the particles comprising the latex along with their particle number and composition. In fact, it is evident, that for the particles of particular composition at given concentrations, the shape of the spectrum is determined by the size distribution only. The size dependence of the light scattering efficiency and the absorption efficiency of a particle is presented in Appendix A.
Figures 2,3,4,5 depict the change in the simulated Uv vis transmission spectrum of styrene-in-water emulsion. Noticeable change in the shape of the simulated spectrum can be observed with the change in the mean diameter and standard deviation of the particle population comprising the latex. Thus, from the simulation studies it can be demonstrated, that the change in the size distribution characteristics of the latex mixture will appreciably reflect upon its measured transmission spectrum.

Similar simulations were carried out for decane-in-water emulsion system with SDBS (Sodium Dodecyl Benzene Sulfonate) as the emulsifier. Decane being a linear hydrocarbon, does not show an absorption signal whereas, the emulsifier SDBS has a distinct signature in the UV region of the spectrum. Performing simulations for such a system enables the study of the changes in the spectral features of the emulsifier as a function of the size distribution characteristics of the emulsion. Figures 6 through 12 depict the results of the simulations for the model emulsion system. The emulsifier spectrum signal was found unique to the size of the particle on which it is distributed (refer Figures 6, 7, 8). Similar observations can be made for the particles with same sizes, but different structures (refer Figures 9,10,11,12).

It is evident from the results of the simulation studies described above, that the shape and the spectral features of simulated transmission Uv vis spectrum of a particle population is extremely sensitive to the size, composition and the structural characteristics of the particles comprising it. A comparison of the simulated spectrum
with the experimentally observed spectrum for the styrene-in-water emulsion SDS (Sodium Dodecyl Sulfate) as the emulsifier revealed that no simulated spectrum of a single particle population matched the shape of the measured spectrum. This indicated the presence of two or more droplet populations that may have contributed to the experimentally observed transmission spectral signal of the styrene emulsion latex.

Simulations were done in order to explore the size characteristics of the constituent populations of the styrene emulsion. The parameters of the simulations were set to generate the transmission spectra of the styrene latex emulsion, such that the simulated spectral features (unique to the size characteristics of the particle populations) were compatible with the observed spectral characteristics of the experimental transmission spectrum. The simulated spectra with spectral features similar to the measured spectrum were then added in proportion, to match its shape (refer Figures 13, 14, 15). Inferences can thus be drawn on the size characteristics of the particle populations comprising this emulsion. The next section describes the theoretical considerations and the mathematical calculations needed to perform the above procedure.

3.2.3 Simulations and Experimental Analysis Performed

In order to compare the shapes of the experimental spectrum and the calculated spectrum (a combination of the simulated spectra of the large and the small particles added in proportion), the following procedure was performed. The simulated spectra having the spectral features compatible with those of the experimental spectrum were
normalized. The appropriate simulated spectrum was normalized by its respective area.

Normalization of the spectrum by its area is done as shown in equation 3.2.

\[
\tau(\lambda) = \frac{\tau_o(\lambda)}{\int_{\lambda_i}^{\lambda_f} \tau_o(\lambda) \, d\lambda}
\]  

(3.2)

where

1. \( \lambda_i \) = Initial wavelength

2. \( \lambda_f \) = Final wavelength

The experimental spectrum is similarly normalized. The simulated spectra of the small and large particle populations were then added in proportion. The shape of the resulting spectrum was then compared with that of the experimental spectrum. The procedure described above is continued until the shapes of the calculated spectra and the experimental spectra were in agreement with each other. Such addition of the normalized simulated spectra (in the required proportions) for matching the shape and the spectral features of the normalized experimental spectrum provides relative concentrations of the populations that comprise the emulsion. A comparison of the shapes of the spectra done in this manner eliminates the effect of the particle number. The procedure for carrying out the above calculations is similar to as given in Appendix B.

It has been demonstrated by Alupoei\textsuperscript{38} that the uncertainty associated with the number of particles in a population is a major contributor to the propagated experimental error and it may bias the conclusions relative to changes in the spectra due to other
variables. It was for this reason that the comparison of the shapes of the experimental and calculated spectra was done by eliminating the effect of the number of particles. The results are shown in Figures 13, 14 and 15. Performing these calculations and comparisons led us to the following inferences.

### 3.3 Inferences Drawn from the Simulation Studies

1. A particle population of the nano-droplets with a mean droplet size of 30 to 100 nm is present during the beginning of the reaction apart from the large monomer droplet population of size range 1 to a few microns in diameter.
2. At least 40 to 50% of monomer is present in the nano-droplets.
3. High interfacial area offered by the nano-droplets owing to small size and high particle number make them a strong candidate for becoming the main reaction loci.
4. There is a need to determine the true parameters of the population of the nano-droplets owing to the spectral contribution of the large particles to the absorption component of the experimental spectrum.

### 3.4 Hypothesis Proposition

The results inferred from the simulation studies provide the basis for proposing the following hypotheses that are necessary to understand the nucleation mechanism in emulsion polymerization.
3.4.1 Hypothesis No 1: Nano-droplets are the most likely nucleation loci in emulsion polymerization reactions.

3.4.2 Hypothesis No 2: The initial emulsification conditions govern the size of the nano-droplets.

3.4.3 Hypothesis No 3: Early time characterization of nano-droplet population and particles in emulsion polymerization, in terms of their size, size distribution and composition can be accomplished using UV vis spectroscopy techniques and model emulsion systems.

The relevance of the hypothesis for elucidating the nucleation mechanism is presented in the next section.

3.5 Relevance of the Proposed Hypotheses for Identifying Nucleation Mechanism

3.5.1 Hypothesis No 1: Nano-droplets are the most likely nucleation loci in emulsion polymerization reactions.

The chapter on literature review describes each of the proposed (and widely accepted to different degrees) theories on nucleation mechanism and the different nucleation locus proposed by each of them. The main nucleation locus in emulsion polymerization process thus continues to remain a subject of active debate.

It is very important that the main reaction locus be identified for studying the nucleation mechanism because it will be at this reaction site that the nucleation
phenomenon will actually occur resulting in the birth of the new particle. The nucleation mechanism will thus be largely governed by the characteristics of the reaction site.

Simulation studies indicated the presence of appreciable amount of dispersed phase in the nano-droplet population and the large interfacial area offered by them. The hypothesis on the nano-droplets being the main nucleation locus is therefore presented.

3.5.2 Hypothesis No 2: The initial emulsification conditions govern the size of the nano-droplets.

Initial emulsification conditions are characterized by the emulsifier concentration, the pH of the suspending medium, the temperature at which the emulsion is prepared and the shear rate of the mixer for a vessel with given mixing characteristics. These conditions have a strong influence on the initial size distribution of the nano-droplets. The initial emulsifier distribution is such, that the free energy due to the large interfacial area present between the two immiscible phases is decreased, thereby imparting stability to the emulsion. The primary function of the emulsifier is to reduce the interfacial tension (commonly denoted by ‘γ’) and hence, the free energy required to disperse a liquid. The expression for the free energy to disperse a liquid of volume ‘V’ with drops of radius R in a solvent is given by

$$\Delta G_{\text{em}} = \gamma \cdot 3 \cdot \left( \frac{V}{R^3} \right)$$

(3.3)

Change in the emulsification conditions cause changes in the dissociation characteristics of the emulsifier and emulsifier efficiency for stabilizing the interfacial
area between the continuous phase and the dispersed phase. In other words, the size, the number and the composition characteristics of the droplet populations comprising the emulsion are affected by the emulsification conditions.

Since the nano-droplets are smaller in size and higher in number than the monomer droplets, the surface area required to be stabilized for the nano-droplet population is expected to be much higher than that of the monomer droplets. It is therefore expected that most of the emulsifier shall be utilized for stabilizing the nano-droplet population. The generation of the electrical double layer around the nano-droplets due to the surfactant distribution before the beginning of the reaction and around the polymer particles after the initiation of the reaction, imparts stability to the reaction mixture by preventing coalescence/coagulation between the droplets/particles. This electric double layer also affects the rate of radical entry by offering resistance to the entering radicals. Thus the density of the emulsifier distributed over the nano-droplets which is a function of initial emulsification conditions, has a profound effect on the rate of nucleation and hence the nucleation mechanism.
**3.5.3 Hypothesis No 3:** Early time characterization of nano-droplet population and particles in emulsion polymerization, in terms of their size, size distribution and composition can be accomplished using Uv vis spectroscopy techniques and model emulsion systems.

According to Lichti\textsuperscript{9,10}, a very fast and reliable measurement technique for characterizing the latex in terms of size and composition is necessary to understand nucleation mechanism. Limitations associated with the currently used experimental techniques by different researchers cause considerable difficulty in early time characterization of the reaction latex and hence valuable information necessary to understand the nucleation mechanism is lost.

Early time characterization of the emulsion mixture present inside the reactor is relevant in undertaking the studies for elucidating nucleation mechanism. This is because it provides the information on the most likely nucleation sites for the emulsion polymerization reaction. Once, the likely nucleation sites are identified, characterizing them on the basis of their size, size distribution, number and composition will provide valuable insight into identifying the mechanism of nucleation.

The compositional characteristics of the droplets during the early stages of the reaction influence the rate of nucleation. The rate capture efficiency of these particles is a function of the concentration of the monomer in them\textsuperscript{1,9}. In the case of micellar
nucleation (assuming it to be the true nucleation mechanism) according to Olayo et al.\textsuperscript{9,10} the radical capture efficiency is a function of the monomer concentration in micelles. According to the homogeneous and coagulative nucleation theories\textsuperscript{2,13,16}, the precursor particles are formed due to the propagation of the initiator radical until they precipitate and later coagulate with other such particles to achieve stability. This theory states that the rate of coagulation (and hence the rate of nucleation) is dependent upon the concentration of the monomer in the precursor particles. Thus, the concentration of the monomer in the precursor particles (assuming homogeneous and coagulative nucleation to be the true nucleation mechanism) or in the micelles (assuming the micellar theory for nucleation is true) presents a very relevant issue that needs to be addressed in order to understand the nucleation mechanism.

It has been pointed out in the earlier section of this chapter, that Olayo et al.\textsuperscript{9,10} used the Morton’s equation as a function of size to calculate the concentration of the monomers in the particles as a function of size. Gilbert\textsuperscript{1} expresses his reticence to use the Morton’s equation to predict the concentration of the monomer inside the particles depending upon the radius for the early reaction times. According to him, the monomer concentration inside the particles show noticeable dependence on the radius of the particle and hence will be significantly less than the value predicted by Morton’s equation. According to Gilbert\textsuperscript{1}, the lack of knowledge of the size dependence of the concentration of the monomer inside the particles makes it difficult to use stage I rate data to gain information about particle formation.
Thus, if the nano-droplets are the true sites for nucleation (proposed as the main hypothesis in this dissertation), then the radical capture efficiency of these nano-droplets (thus converting the nano-droplets to particles) and their nucleation rate will be dependent upon their size and the concentration of the monomer in them. Hence, it is important that the compositional characteristics of the likely reaction sites as a function of their size and the changes they undergo over time as the reaction progresses be investigated.

This research effort therefore takes the approach of characterizing the latex mixture present in the reactor before the reaction is initiated (essentially a liquid-liquid emulsion system at early times) in order to understand the nucleation.

The results from the simulation studies showed that the shape of the simulated transmission Uv vis spectra of styrene in water emulsion changed appreciably with the change size distribution characteristics of the droplet populations that comprise the emulsion (refer Figure 2 through Figure 5). Similar observations were made for the simulation studies involving Decane in water emulsion with Sodium Dodecyl Benzene Sulfonate (SDBS as the emulsifier). The conclusions from the works of Maria Celis\textsuperscript{36} stated that the sample integrity is maintained throughout successive dilutions. It was thus inferred that the spectroscopic tools could be implemented to characterize the reaction mixture during early times to obtain the information required for identifying the nucleation mechanism.
In order to establish the relationship between the size of the reaction site and its compositional characteristics, it is necessary to characterize the droplet populations in terms of their size and compositions. In order to achieve this, the information on the particle size distributions (PSDs) of the reaction loci in the early stages of the reaction needs to be coupled with emulsifier and oil phase mass balance. Use of the model emulsion system comprised of molecules with the similar dispersion properties but different optical properties is therefore considered.

The study of the distribution of the emulsion component of interest was undertaken by selecting the appropriately labeled compound. Information on the composition of the droplet populations comprising the emulsions and their size characteristics can thus be obtained by taking this approach.

3.6 Conclusion

Simulation studies indicate the nano-droplet populations to be the prime candidates for being the most likely nucleation loci. The size and the compositional characteristics of the nano-droplet populations are expected to change with the change in the emulsification conditions.

The Uv vis spectroscopic techniques can be used to characterize the liquid-liquid emulsion present in the reactor at time zero in terms of number, size distribution and composition of each of the droplet populations comprising it. Appropriate model
emulsion system can be employed in order to achieve this objective. Relevant information on size and compositional characteristics of the most likely nucleation loci that is necessary to elucidate the nucleation mechanism in emulsion polymerization processes can be obtained by following this approach.

Details pertaining to the experiments with the model systems and justification for their consideration are provided in the experimental section.
Figure 2 Change in the Shape of the Simulated Transmission Spectra of the Nano-droplet Population of Styrene in Water Emulsion as a Function of its Standard Deviation and Constant Mean Diameter (Dn)

Figure 3 Change in the Shape of the Simulated Transmission Spectra of the Nano-droplet Population of Styrene in Water Emulsion as a Function of its Mean Diameter (Dn)
Figure 4 Change in the Shape of the Simulated Transmission Spectra of the Large Droplet Population of Styrene in Water Emulsion as a Function of its Mean Diameter (Dn)

Figure 5 Change in the Shape of the Simulated Transmission Spectra of the Large Droplet Population of Styrene in Water Emulsion as a Function of its Standard Deviation
Figure 6 Comparison of the Simulated Transmission Spectra of Decane in Water Emulsion (with SDBS Emulsifier) for Droplet Populations of Different Sizes
Figure 7 Effect of Particle Size for Decane in Water Emulsion with SDBS as the Emulsifier on the Simulated Transmission Spectra for the Latex Consisting of Small Droplets (Amplified Lower Wavelength Region)

Note: The emulsifier signal looks very different when the emulsifier is distributed over small droplets than when it is in solution. Note the change in the spectral features of the emulsifier. Emulsifier spectral features are unique to the size of the droplets over which they are distributed.
Figure 8 Comparison of the Effect of Particle Size for Decane in Water Emulsion with SDBS as the Emulsifier on the Simulated Transmission Spectrum of the Emulsifier Distributed on the Droplets (Amplified Lower Wavelength Region)

Note: Emulsifier spectral features are unique to the size of the droplets over which they are distributed.
Figure 9 Comparison of the Effect of the Particle Structure on the Simulated Transmission UV-vis Spectrum of the Latex for the Same Droplet Size (Small Droplet Size 10 to 30nm in Diameter)
Figure 10 Comparison of the Effect of the Particle Structure on the Simulated Transmission UV-vis Spectrum of the Latex for the Same Droplet Size of Range 10 to 30 nm (Amplified Lower Wavelength Region)

Note: The emulsifier spectral features are unique to the particle structure.
Figure 11 Comparison of the Effect of the Particle Structure on the Simulated Transmission UV vis Spectrum of the Latex for the Same Droplet Size (Bigger Droplets of Size Range 50nm to 100nm in Diameter Dn)
Figure 12 Comparison of the Effect of the Particle Structure on the Simulated Transmission UV vis Spectrum of the Latex for the Same Droplet Size of Range 50 to 100 nm (Amplified Lower Wavelength Region)

Note: The emulsifier spectral features are unique to the particle structure.
Figure 13 Comparison of the Shape of the Normalized Experimental Spectrum with that of the Simulated Transmission Spectrum of Large and Small Droplets of Different Mean Diameters (Dn) added in Equal Proportions

Figure 14 Comparison of the Shape of the Simulated Transmission Spectrum of Large Droplets about 3 microns and Small Droplets of 30nm Mean Diameter (Dn) added in Different Proportions and the Normalized Experimental Spectrum

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Figure 15 Comparison of the Shape of the Simulated Transmission Spectrum of Large Droplets about 3 microns and Small Droplets of 50nm Mean Diameter (Dn) added in Different Proportions and the Normalized Experimental Spectrum
CHAPTER 4: EXPERIMENTAL WORK UNDERTAKEN

4.1 Introduction

Simulation studies presented in Chapter 3 indicated that the reaction mixture at time zero could be characterized using UV vis spectroscopic techniques. The preliminary studies suggested the presence of significant amount of the dispersed phase in the nano-droplet population. The nano-droplet population offered high interfacial area (owing to their small size and high particle number). These inferences resulted in the formulation of the hypothesis proposing the nano-droplets to be the main nucleation loci in emulsion polymerization processes.

In order to test the above hypothesis, experimental efforts were undertaken to characterize the reaction mixture at time zero condition in terms of number, size characteristics and composition of each of its comprising droplet populations. Experiments were performed using a non-reacting model emulsion system having similar dispersion characteristics as that of the original monomer in water emulsion but different optical properties. These experiments were performed to investigate the effects of initial emulsification conditions on the size and the compositional characteristics of the dispersed phase. Spectroscopic techniques were used to characterize the dispersed phase of the model emulsion system.
Details of the experimental work performed with the model emulsion system and the rationale for taking this approach are presented in this chapter.

4.2 Rationale for Using Model Emulsion System

Results inferred from the simulation studies presented in Chapter 3 (Figures 13 through 15) indicated a presence of more than one population of the dispersed phase of the emulsion at time zero of emulsion polymerization process. For the identification of the most likely nucleation locus, it is important that each population of the dispersed phase be characterized in terms of its size, number and composition. Such characterization of the dispersed phase requires information on the distribution of each component (oil and emulsifier) in the dispersed phase population. Surfactant distribution determines the composition and the feasibility of the existence of the droplet population having particular size characteristics. Hence, the study of surfactant distribution is important for identification of the most likely nucleation locus. For obtaining the information on surfactant distribution, it is necessary to identify the surfactant signal and determine its contribution to the measured spectra. Performing experiments with monomer emulsion systems makes it difficult to identify the surfactant signals since the monomers (e.g. Styrene) have strong absorption peak in the UV region overlapping the signal of the surfactant. It was for this reason that the experiments with model emulsion systems consisting of components with similar physico-chemical properties but different optical properties as proposed in the Chapter 3 of this dissertation.
Under similar emulsification conditions (temperature, pH, surfactant concentration), dispersed phases having similar physico-chemical properties (viscosity, vapor pressure, density, interfacial tension) display similar dispersion characteristics\(^3\). The components of the model emulsion system selected to imitate the dispersion characteristics of the reaction latex mixture at time zero therefore have their physico-chemical properties similar to the respective components of the reaction latex mixture present inside the reactor at time zero. The distribution of the components of emulsion system (namely emulsifier, oil phase and continuous phase) under consideration can be studied by the use of appropriately labeled compounds.

The optical properties of the selected components for the model system are different from those of the respective components of the reaction latex mixture such that good contrast for the spectroscopy measurement is provided. The optical properties of the compounds of interest are reported in Appendix C. The investigation of the distribution of the emulsion component of interest (emulsifier or oil) is possible by identifying and evaluating its spectral contribution to the measured spectrum. The primary advantage of using the non-reacting model emulsion system is the removal of the time constraint for immediate sampling of the monomer emulsion mixture, present inside the reactor at time zero.
4.3 Experiments with Model System

In this section, the materials comprising the model system are specified. The experimental design strategy with the objective of systematically investigating the effect of the different manipulated variables under consideration on the emulsion characteristics is explained. A justification for selecting the temperature, pH of the suspending medium and the surfactant concentration as the manipulated variables describing the initial emulsification conditions for studying their effects on the emulsion characteristics is provided.

4.3.1 Materials and Methods

4.3.1.1 Materials

The model emulsion system employed model molecules with emulsifier (Sodium Dodecyl Benzene Sulfonate) having a distinct absorption peak in the Uv vis signal of its transmission spectrum. Decane was used as the transparent oil phase (dispersed phase) to mimic the dispersion behavior of the monomers owing to its similar physico-chemical properties with styrene, butyl methacrylate etc. The reagents were obtained from Sigma Aldrich. In Table 4.1, the comparisons of the approximate values of the physical properties of decane\textsuperscript{40,41,43,46,47} styrene\textsuperscript{40,41,42,44} and butyl methacrylate\textsuperscript{21,40,41,45,48} are shown.
Table 4.1 Comparison of the Physical Properties of Styrene, Butyl Methacrylate and Decane

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Styrene</th>
<th>Butyl Methacrylate</th>
<th>Decane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>0.906</td>
<td>0.889</td>
<td>0.73</td>
</tr>
<tr>
<td>Vapor pressure (mm Hg)</td>
<td>5</td>
<td>4.9</td>
<td>1.4</td>
</tr>
<tr>
<td>Interfacial Tension (dynes/cm)</td>
<td>27.7</td>
<td>28</td>
<td>30.4</td>
</tr>
<tr>
<td>Viscosity (centipoise)</td>
<td>0.675</td>
<td>0.832</td>
<td>0.863</td>
</tr>
</tbody>
</table>

Phosphate buffer saline (PBS) was used as the continuous phase. The emulsions were prepared in a buffer of known pH as the suspending medium. This was done to explore the dispersion characteristics of the oil phase as a function of pH since the emulsifier efficiency was expected to change as a function of the pH of the suspending medium. The pH of the PBS buffer was decreased by the addition of HCl (pH 1) and increased by the adding NaOH of pH 13.

4.3.1.2 Methods

The emulsion was prepared under different conditions as described in section 4.3.6 and the transmission Uv vis spectrum of the diluted emulsion was recorded. The buffer was prepared at room temperature in such a way that it would possess the desired pH at elevated temperatures. Three replicate measurements of the transmission spectrum were obtained for each of the experiments. The mean transmission spectrum for each experiment performed was obtained. The 95% confidence intervals for the optical densities at each wavelength were calculated. In comparing the shape of the spectra, the
optical density for any particular wavelength lying outside the upper and lower limits of the confidence intervals was considered to be an outlier since it was considered to be statistically different. The spectral results are shown in Appendix E. Three replicate experiments were performed at the room temperature. The results of the transmission spectra so obtained were compared and are shown in Figure 17.

The emulsion was characterized in terms of the particle size distribution, particle number and particle composition for each population of the dispersed phase comprising it from its transmission Uv vis spectrum, using turbidity equation (equation 3.1). The algorithms developed in-house performed constrained optimization for characterizing the emulsion present inside the reactor from its transmission spectrum. The mass balance on the oil was the constraint that was implemented for resolving the spectrum to characterize the emulsion. The transmission Uv vis spectra of the emulsion could only be partially resolved (from 280 to 820 nm) for characterization purposes since the spectral features of the emulsifier changed considerably in the lower wavelength region. In order to resolve the complete Uv vis transmission spectrum of the emulsion in the model system, more work needs to be done on the estimates of the optical properties of the surfactant. The work performed on for estimating the optical properties of the surfactant during this research is reported in Appendix C.
4.3.2 Equipment and Experimental Setup

The emulsion was prepared in a 500 ml glass reactor. A temperature controller supplying the necessary amount of heat to the heating jacket electrically, maintained the desired temperature of the emulsion inside the reactor. Two baffles for breaking the vortex caused as a result of agitation were attached to the covering lid. The covering is placed on the reactor such that the stirrer rod passes through the central opening of the lid. The stirrer rod fits into the chuck of the motor. The emulsion is kept under constant agitation with the help of a stirrer rotating 500 RPM. The RPM was verified with a stroboscope for each experiment. A sample slip-stream was drawn continuously from the reactor with the help of the sample pump and sent to the dilution system where it was diluted with the suspending medium. The temperature of the diluent was maintained the same as the emulsion with the help of another temperature control system. This temperature control system consisted of an electrically powered heating mantle for maintaining the temperature of the diluent. The temperature sensing thermocouple for this temperature control system was immersed in the diluent (suspending medium is used as the diluent).

The sample emulsion stream was drawn from the reactor and sent to the dilution system where it came in contact with the diluent. The transmission spectrum of this diluted emulsion was recorded at desired sample times. The flow rates of the diluent stream and the sample slip-stream were such that the transmission spectrum of the diluted emulsion was within the linear range of the spectrometer (optical density below 1). The
The complete protocol for operating the dilution system is presented in Appendix I. The spectrometer used was a Hewlett Packard spectrometer model number HP8452A with a resolution of 2 nm. The sample cell holder of the Hp spectrometer was maintained at the desired temperature with the help of another electrical temperature controller manufactured by Perkin Elmer (C5700820). All the hoses and tubes were insulated with glass fiber insulation to minimize the heat loss. The pH of the suspending medium and the diluent was monitored with the help of the pH meter manufactured by Fisher (Fisher accumet model number 610). The custom-made aluminum surface-tensiometer probes through which the nitrogen is bubbled are placed in the reactor. The interfacial tension of the emulsion is measured with the surface-tensiometer. Figures 18 and 19 show the schematic of the entire experimental setup.

### 4.3.3 Experimental Design Strategy

The experiments performed with the model systems were designed to explore the effects of the initial emulsification conditions. The variables describing the initial emulsification conditions are listed as follows:

1. Surfactant concentration,
2. Temperature,
3. pH.

The effect of the above mentioned variables on the size distribution characteristics of the dispersed phase of the emulsion in the model system are studied. These variables are expected to affect the emulsifier behavior in a micellar solution. Change in the
emulsifier behavior is expected to affect characteristics of the dispersed phase of the
emulsion since the characteristics of the dispersion (interfacial area stabilized,
composition of the dispersed phase, size distribution of the droplets of the dispersed
phase population, decision on the continuous phase etc) are decided by the emulsifier
characteristics. The justification for the selection of the above-mentioned variables for
studying their effect on the dispersion characteristics is provided in the next section.

4.3.4 Relevance of the Experimental Variables

4.3.4.1 Effect of Surfactant Concentration on Initial Distribution of the Particle
Populations

Preparation of the emulsion involves usage of shear force to achieve the
dispersion of one liquid phase into another. The reduction of the shear force requirement
for achieving dispersion and maintaining the stability of the emulsion is the primary
function of the surfactant (emulsifier).

The emulsifier concentration affects its dynamic characteristics thereby
affecting the characteristics of the stable dispersed phase. The stability of the dispersed
phase is expected to increase with the increase in the emulsifier concentration and hence
is expected to reflect upon compositional, particle number and the particle size
distribution characteristics of the dispersed phase. Thus the emulsifier concentration
governs the characteristics of the dispersed phase and the characteristics of the most
likely nucleation locus. It is therefore important to explore the effect of the surfactant
concentration on the initial distribution of droplet populations of the dispersed phase.
4.3.4.2 Effect of Temperature on Initial Distribution of the Particulate Populations

Change in temperature alters the interfacial tension. The surface tension of a micellar solution decreases with increasing temperature since the effectiveness of the surfactant is dependent on the temperature. This change in the surfactant kinetics causes a change in the adsorption characteristics of emulsifier on the dispersed phase and the viscosity of the emulsion \(^{39}\). The characteristics of the dispersed phase of the reaction mixture are thus expected to change by the changes in temperature thereby potentially affecting the choice of the most likely nucleation locus. Hence it is necessary to investigate the effect of the temperature on the size and composition characteristics of the dispersed phase.

4.3.4.3 Effect of pH on Initial Distribution of the Particulate Populations

The change in pH of the emulsion affects the dissociation characteristics of the emulsifier. The interfacial area between the continuous and the dispersed phase is dependent upon the dissociation characteristics of the emulsifier. Hence the change in the pH of the suspending medium is going to affect the size and the composition characteristics of the dispersed phase, which in turn is very critical in deciding the most likely nucleation locus. It is therefore necessary to investigate the effect of pH on the characteristics of the droplet populations of the dispersed phase. In order to observe the effects of surfactant concentration, temperature and pH of the suspending medium on the emulsifier characteristics (since the emulsifier characteristics will affect the characteristics of the dispersion), preliminary experiments were performed on the
surfactant micellar solutions. The surfactant micellar solutions of Sodium Dodecyl Benzene Sulfonate (SDBS) was studied spectroscopically to observe the micelle forming behavior of the surfactant molecules at different conditions of surfactant concentration, temperature and pH. The concentration of SDBS was well above its critical micellar concentration and hence, was considered as a dispersion solution of aggregated surfactant molecules (micelles). From the turbidity equation (equation 3.1) it can be inferred that the change in the shape of the transmission Uv vis spectrum of the micellar solution reflects upon the change in the size and number characteristics of the micelles formed. Changes in the aggregation behavior of the surfactant molecules for forming micelles is thus indicated by the change in the shape of the transmission Uv vis spectrum of the micellar solution. The differences in the shapes of the transmission Uv vis spectra with the change in the surfactant concentration, temperature and the pH of the suspending medium are reported in Appendix D. From the results obtained form the preliminary experiments, it can be inferred that the surfactant concentration, temperature and pH of the suspending medium affect the emulsifier behavior. The changes in the emulsifier behavior as a function of the mentioned variables are expected to affect the size, number and composition characteristics of the droplet populations of the dispersed phase of the emulsion.

4.3.5 Experimental Design Strategy

It has been mentioned in the earlier section that the surfactant concentration, temperature and pH of the suspending medium are the three variables describing the
initial emulsification conditions, whose effects on the characteristics of the dispersed phase need to be investigated. The experiments were therefore designed as a $2^f$ factorial design ($f = 3$). However, the design of the experiments was not symmetric since the extremes of each of the variables in order to see significant differences in the shapes of the transmission spectra of the emulsions were needed to be explored. This resulted in a skewed design of experiments with two levels and three variables. The experimental conditions for each experiment are enumerated in Table 4.2.

Figure 16 is a pictorial representation of the experimental design strategy.

The upper and the lower levels of the control variables of interest are explained as follows:

4.3.5.1 Surfactant Concentration

The higher level of the surfactant concentration was chosen to be 0.046 surfactant/oil ratio in the emulsion recipe while the lower limit of the surfactant concentration was chosen to be 0.0154 surfactant/oil ratio. In both the recipes, for the emulsion prepared, surfactant concentration was higher than the critical micellar concentration. These levels of surfactant concentrations were selected such that there was enough concentration difference between the higher and the lower levels of the surfactant concentrations and yet both of the extremes were above CMC. The presence of micelles in both the recipes was thus ensured and hence the change in the emulsion characteristics in the presence of the micelles could be studied. The higher limit of the surfactant
concentration was almost 1.3 times that of the surfactant concentration used in the standard recipe of the emulsion polymerization experiments\textsuperscript{1}. The lower limit was less than half the surfactant concentration of the standard recipe mentioned above.

4.3.5.2 Levels of pH

The pH levels of the suspending media were decided based upon the dissociation characteristics of the surfactant. The pKa value of the surfactant was expected to be closer to that of the Dodecyl Benzene Sulfonic Acid. The pKa value for 1-[(4-butylphenyl) sulfanyl] trioxidane, an organic compound, having very similar structure to the Dodecyl Benzene Sulfonic Acid was calculated to be 6.91 with an error of 0.41. This pKa was calculated using the software developed by the ACD\textsuperscript{50,51} laboratory. Structural similarity between Dodecyl Benzene Sulfonic acid and 1-[(4-butylphenyl) sulfanyl] trioxidane justified the expectation for the closeness in their pKa value. The lower limit of the pH of the suspending medium was selected to be 2 (much lower than its expected pKa value). This was done so that the effect of the non-dissociated surfactant on the emulsion formation could be observed. The higher limit of the pH was chosen to be 10. The surfactant was expected to dissociate completely at 10 pH. Thus, the effect of the completely dissociated surfactant on the emulsion formation can be observed. The comparison of the emulsifier capability when dissociated partially to that when dissociated completely can thus be studied.
4.3.5.3 Temperature

The higher and lower limits of temperature were initially chosen to be 60 degree Celsius and 50 degree Celsius respectively because this is the temperature range typically maintained for emulsion polymerization reactions. However, little difference in the shape of the spectrum was observed within this temperature range of interest for the first six experiments in the design. Therefore, the lower limit of the emulsion preparation was chosen to be 22°C (room temperature) thus skewing the experimental design strategy.

4.3.6 Experimental Procedure

150 ml of the suspending medium is added to the 500ml glass reactor placed in the heating jacket of the temperature controller that was used to control the temperature of the emulsion in the reactor. To the suspending medium was added 30 ml of surfactant solution. This surfactant solution was made by the addition of the surfactant in required quantity as per the recipe to 30 ml of the suspending medium. The thermocouple for sensing the temperature inside the reactor was then lowered inside the reactor along with the surface tensiometer probes. The contents in the reactor were then heated until the desired temperature set point was reached. 160 ml of decane was then added to the reactor and this mixture was then subjected to continuous agitation to form emulsion. After ensuring that the stability of the emulsion was achieved as described in the next paragraph, it was sampled for analysis purposes. The sample slip-stream of the emulsion inside the reactor was diluted by pumping it into the dilution system with a rotary
peristaltic pump. This dilution of the sample stream enabled the measurement of its transmission spectrum.

To determine the time required to stabilize the emulsion, another experiment in which the emulsion was prepared as above was performed. The pH of the suspending medium of the emulsion was maintained at 7 pH. The Surfactant to Oil ratio in the recipe was maintained at 0.0307 as per the standard recipe. The experiment was carried out room temperature. The emulsion was sampled off line at varying time intervals. The shapes of the transmission spectra of the emulsion sampled at different times were compared by comparing the spectra normalized by their respective areas (refer Appendix F). It was observed that the shape of the transmission spectrum of the emulsion changed as a function of time indicating the change of the particle size distributions of the particulate populations comprising the emulsion. After about two hours fifteen minutes of the addition of decane and beginning of the agitation action, the shape of the spectrum remained constant indicating that the stability of the emulsion had been achieved. The change in the shape of the spectra of the emulsion as a function of time is represented in Appendix F. The deconvolution results of the Uv vis transmission spectra of the emulsion before stabilization are presented in Chapter 5 along with the pertinent discussion.

4.4 Data Analysis

Cardenas, Shastry and Garcia-Rubio\textsuperscript{52} describe the transmission spectroscopic techniques as an analysis tool for characterization of emulsion latex in great detail. The
measured transmission spectra of the emulsions is deconvoluted using the software developed in-house$^{34,35}$ to obtain information on the particle composition, particle number and the particle size distribution of each of the particle population present in the emulsion. The algorithms were based on the turbidity equation (equation 3.1). The optical properties of the oil phase at appropriate temperatures were used as the inputs for executing these algorithms.

The estimation of the optical properties is presented in Appendix C. In the section 4.3.1.2, the analysis of the transmission UV vis spectral data of the emulsion using the turbidity (equation 3.1) to obtain the information on the particle number, particle size distribution and composition of the particle composition comprising it has already been described. The emulsion spectra were analyzed from the wavelength region of 280 to 820 nm to determine the size distribution characteristics of the droplet populations comprising the emulsion. Weight fraction of the dispersed phase in the small nano-droplet population was calculated from the transmission spectrum for each emulsification condition along with the number of particles and the size distribution characteristics of each of the droplet population. The results are reported in the next chapter.
### Table 4.2 Experimental Conditions

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temperature in °C</th>
<th>pH</th>
<th>Surfactant/ Oil ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment 1</td>
<td>50</td>
<td>2</td>
<td>0.0154</td>
</tr>
<tr>
<td>Experiment 2</td>
<td>60</td>
<td>2</td>
<td>0.0154</td>
</tr>
<tr>
<td>Experiment 4</td>
<td>60</td>
<td>10</td>
<td>0.0154</td>
</tr>
<tr>
<td>Experiment 5</td>
<td>50</td>
<td>2</td>
<td>0.046</td>
</tr>
<tr>
<td>Experiment 6</td>
<td>60</td>
<td>2</td>
<td>0.046</td>
</tr>
<tr>
<td>Experiment 7</td>
<td>22</td>
<td>10</td>
<td>0.046</td>
</tr>
<tr>
<td>Experiment 8</td>
<td>60</td>
<td>10</td>
<td>0.046</td>
</tr>
</tbody>
</table>

![Figure 16 Experimental Design Strategy](image)

Figure 16 Experimental Design Strategy
Figure 17 Results Obtained from Replicate Experiments at Center-point
Figure 18 Schematic of the Reaction Vessel Assembly for the Experiments Performed
Figure 19 Dilution System Assembly for Spectroscopy Measurements
Figure 20 Reactor for the Experiments with Model Molecules

Figure 21 Reactor Assembly Setup with Temperature Control Jacket for the Reactor and Surface Tensiometer Probes
Figure 22 Dilution System Assembly to Acquire Transmission Spectra

Figure 23 System Setup for Experiments with Model System

Note: Temperature controllers for the diluent and the reactor can be seen along with the reaction setup assembly, surface tensiometer probes and the dilution system.
Figure 24 Temperature Control System for the Sample Holder of the Spectrometer

Figure 25 Entire Setup for Experiments with Model System
Figure 26 pH Meter to Measure the pH of the Suspending Medium
CHAPTER 5: RESULTS AND DISCUSSIONS

5.1 Introduction

This section reports and discusses the results obtained from the experiments performed as described in Chapter 4. The simulation studies described in the Chapter 3 of this dissertation indicate the presence of two or more populations of the droplets present in the cuvette. The results inferred from the simulation studies led the formulation of the proposed hypothesis on the presence of small nano-droplet population of size range 30 to 100 nm in diameter in the emulsion, along with the large monomer droplet population of size range 2 to 3 microns. The spectral data of the emulsions prepared at different conditions of temperature, surfactant concentration and pH of the suspending medium were analyzed to determine the number of populations of the dispersed phase and their size characteristics. This analysis was done by spectroscopy. In order to obtain information of the characteristics of the dispersed phase, the spectral signal from the wavelength range, 280 to 820 nm was analyzed. In this chapter, the effects of each of the emulsification condition on the size characteristics of the particle population are presented and discussed. Before recording the transmission Uv vis spectra of the emulsions for performing the analysis, it was ensured that the emulsion had achieved stability.
This was made possible by pre-determining the time required for the emulsion to achieve stability as described in section 4.3.6. The spectral data reported in Appendix F was deconvoluted using the turbidity equation (equation 3.1) as described in section 4.3.1.2. The results are reported in Table 5.1. It can be observed from the results that the size distribution characteristics of the small particle population remain fairly constant before the emulsion was stabilized while the mean diameter of the large particle population changed significantly. The standard deviation of the large particle population was also observed to be constant. The percentage of the dispersed phase in the small particle population seemed to be changing until emulsion attained stability. The weight percent of oil in the dispersed was constant after the stability of the emulsion was achieved.

Table 5.1 Results Obtained by Deconvoluting the Uv vis Transmission Spectra of the Emulsion Before Stability

<table>
<thead>
<tr>
<th>Time</th>
<th>Mean diameter of small Particle Population</th>
<th>Std dev Small particle Population</th>
<th>Mean diameter of Large particle Population</th>
<th>Std dev Large particle Population</th>
<th>Wt% of Oil in Small Particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 minutes</td>
<td>32</td>
<td>0.1</td>
<td>5202</td>
<td>0.6</td>
<td>54.4</td>
</tr>
<tr>
<td>20 minutes</td>
<td>30</td>
<td>0.1</td>
<td>6490</td>
<td>0.5</td>
<td>51.9</td>
</tr>
<tr>
<td>45 minutes</td>
<td>31</td>
<td>0.1</td>
<td>5512</td>
<td>0.6</td>
<td>44.1</td>
</tr>
<tr>
<td>1 hour</td>
<td>32</td>
<td>0.1</td>
<td>4875</td>
<td>0.5</td>
<td>57.2</td>
</tr>
<tr>
<td>1 hour 45 min</td>
<td>32</td>
<td>0.1</td>
<td>5713</td>
<td>0.6</td>
<td>42.8</td>
</tr>
<tr>
<td>2 hours 15 minutes</td>
<td>30</td>
<td>0.1</td>
<td>3759</td>
<td>0.6</td>
<td>70.7</td>
</tr>
</tbody>
</table>
Table 5.2 lists the effect of the manipulated variables on the characteristics of the dispersed phase populations namely, number of populations of the dispersed phase, their size characteristics and the percentage of the dispersed phase contained in each of the population. In Table 5.3 the summary of the experimental results is reported. Table 5.4 reports the comparison between the results obtained with offline and online spectra of the decane-in-PBS buffer emulsion. Results obtained by deconvoluting the transmission spectrum of the styrene-in-water emulsion before the beginning of the polymerization reaction are also presented in Table 5.4. The spectrum of styrene was deconvoluted for the wavelength region 200 to 820 nm. Excellent fit was obtained between the estimated and the measured spectra of the styrene in water emulsion (refer Figure 113). The comparison between the experimental spectra and the calculated spectra are presented in Figures 27 through 33. Figures 36 through 44 elucidate the effect of different emulsification conditions on the mean diameter, standard deviation of the nano-droplet population along with the weight percent of the dispersed phase in them. Change in the size characteristics of the large droplet population as a function of emulsification conditions are shown in Figures 45 and 46. The continuous lines have been placed to suggest the main trend in the data.

For each of the experiments, an analysis was performed on the surfactant distribution over the particle populations of the dispersed phase. The results are tabulated in Table 5.5. Table 5.6 reports the area required to be stabilized per molecule for a particle population of the given size characteristics to exist. The smaller the area
required for the stabilization of the area per molecule of the surfactant, higher is the probability of the stability of the particle and hence, higher the probability of its existence.

5.2 Effects of the Manipulated Variables

5.2.1 Effect of Surfactant Concentration

The effect of the surfactant to oil ratio on the mean and the standard deviation of the nano-droplet population are shown in Figures 39 and 40 respectively for different conditions of pH and temperature. The effect of the surfactant to oil ratio on the wt% of the dispersed oil phase in the nano-droplet population at different conditions of pH and temperature is shown in Figure 41. It was observed that the mean diameter of the small particle population was influenced by the surfactant concentrations. The mean diameter of the small particle populations at high surfactant to oil ratio was around 30 nm in diameters whereas for low surfactant to oil ratio, it was around 100 to 110 nm in diameter. The number of particles of the small particle population was found to be much higher for the emulsion recipe having higher surfactant to oil ratio than the one having lower surfactant to oil ratio. The percentage of the dispersed phase in the nano-droplet population is greatly influenced by the surfactant to oil ratio. At low surfactant to oil ratios, for different conditions of pH and temperatures, only 18% of the dispersed phase was present in small particles while for the emulsion recipes having higher surfactant to oil ration, more than 70 to 80% of the dispersed phase was present in the nano-droplet population. The surfactant to oil ratio however did not have much effect on the size
characteristics namely the mean diameter and the standard deviation of large droplet population (refer Figures 45 and 46).

5.2.2 Effect of Temperature

The effect of the temperature on the mean and the standard deviation of the nano-droplet population are shown in Figures 42 and 43 respectively for different conditions of surfactant to oil ratios and pH. The effect of temperature on the wt% of the dispersed oil phase in the nano-droplet population at different conditions of pH and surfactant to oil ratios is shown in Figure 44. The effect of temperature on the mean diameter of the nano-droplet population at both high and low surfactant to oil ratio for the suspending medium with low pH is negligible. However for high differences in temperature, as shown in Figure 42 for a suspending medium with high pH, the mean diameter decreased slightly with the increase in temperature but was still within the limits of 95% CI. This indicated that the change in the mean diameter is negligible as a function of temperature for suspending medium with high pH. The standard deviation of the small particle population was also within the limits of 95% CI for high and low surfactant to oil ratio recipes for low pH of the suspending medium (refer Figure 43). At high pH of the suspending medium a higher estimate of the standard deviation of the estimate of small particles was observed at low temperatures. The temperature effect on the percentage of the dispersed phase in the mass fraction of the small particle population is almost negligible for the emulsion recipe having high surfactant to oil ratio for both high and low pH of the suspending medium.
5.2.3  Effect of pH

Figures 36 and 37 depict the effect of pH on the mean diameter, standard deviation of the nano-droplet population respectively at different conditions of surfactant to oil ratios. Figure 38 depicts the effect of pH on the weight percent of the dispersed phase in the nano-droplet population for different surfactant to oil ratios. Figures 36 suggests that the mean diameter of the nano-droplet population for the emulsion recipes with low surfactant to oil ratios remains unaffected at high temperatures by the change in the pH of the suspending medium. Similar observation was made with respect to the effect of pH of the suspending medium on the mean diameter at high temperatures for the emulsion recipe with high surfactant/oil ratio. Standard deviation of the small particle population remained unchanged as a function of pH of the suspending medium for the emulsion recipes with both high and low surfactant to oil ratios, at high temperatures (refer Figure 37). Higher variability in the estimated standard deviation of the small particle population was observed for the suspending medium with low pH. The percentage of the dispersed phase in the small particles for both the cases of surfactant to oil ratio in the emulsion recipe seemed to be unaffected by the pH of the suspending medium (refer Figure 38).

The mean and the standard deviation of the large droplet population was unaffected by the emulsification conditions (refer Figures 45 and 46).
The results described above are conveniently tabulated as in Table 5.2. The effects of the manipulated variables viz temperature, pH and surfactant concentration on the size distribution characteristics namely the mean \((\mu_s)\) and the standard deviation \((\sigma)\) of the nano-droplet population and on the weight percent of the oil contained in them (represented as ‘%’) are summarized in Table 5.2. The effect of an emulsification condition on the characteristics of the nano-droplet population is regarded to be appreciable when the observed changes are beyond the 95% CI of the estimates respectively. Due to the skewed design of experiments, the isolation of a particular effect on the characteristics of the small particle population at given conditions was not possible in certain cases and hence could not be expressed.

The effects of the variables at the specified conditions on these characteristics are denoted as:

1. \(I\) = Appreciable increase with the increase of the effect;
2. \(D\) = Appreciable decrease with the increase of the effect;
3. \(N\) = Not appreciable;
4. \(N_{PE}\) = Not possible to express
### Table 5.2: Effects of the Manipulated Variables on the Nano-droplet Population of the Dispersed Phase

<table>
<thead>
<tr>
<th></th>
<th>Effect of pH</th>
<th>Effect of Temperature</th>
<th>Effect of Surfactant Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At low Surfactant Conc</td>
<td>At high Surfactant Conc</td>
<td>At low pH</td>
</tr>
<tr>
<td></td>
<td>For High Temp µs N</td>
<td>For High Temp µs N</td>
<td>For High Temp µs N</td>
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<tr>
<td></td>
<td>σ N</td>
<td>σ N</td>
<td>σ N</td>
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<tr>
<td></td>
<td>% N</td>
<td>% N</td>
<td>% I</td>
</tr>
<tr>
<td></td>
<td>% NPE µs N</td>
<td>% NPE µs N</td>
<td>% NPE µs N</td>
</tr>
<tr>
<td></td>
<td>σ NPE µs N</td>
<td>σ NPE µs N</td>
<td>σ NPE µs N</td>
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<tr>
<td></td>
<td>% NPE µs N</td>
<td>% NPE µs N</td>
<td>% NPE µs N</td>
</tr>
<tr>
<td></td>
<td>% NPE σ N</td>
<td>% NPE σ N</td>
<td>% NPE σ N</td>
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<td>% NPE σ NPE</td>
<td>% NPE σ NPE</td>
<td>% NPE σ NPE</td>
</tr>
<tr>
<td></td>
<td>For Low Temp µs NPE</td>
<td>For Low Temp µs NPE</td>
<td>For Low Temp µs NPE</td>
</tr>
<tr>
<td></td>
<td>σ NPE µs N</td>
<td>σ NPE µs N</td>
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<td>% NPE µs N</td>
<td>% NPE µs N</td>
</tr>
<tr>
<td></td>
<td>% NPE σ N</td>
<td>% NPE σ N</td>
<td>% NPE σ N</td>
</tr>
<tr>
<td></td>
<td>% NPE σ NPE</td>
<td>% NPE σ NPE</td>
<td>% NPE σ NPE</td>
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</table>
Table 5.3 Summary of Experimental Results

<table>
<thead>
<tr>
<th>Experiment Conditions</th>
<th>Mean diameter of small particle population</th>
<th>Standard deviation of small particle population</th>
<th>Mean diameter of large particle population</th>
<th>Standard deviation of large particle population</th>
<th>Wt% of decane in small particle population</th>
</tr>
</thead>
<tbody>
<tr>
<td>T=50 C S/O=0.0154 pH=2</td>
<td>109</td>
<td>0.1</td>
<td>3409</td>
<td>0.6</td>
<td>18.0</td>
</tr>
<tr>
<td>T=50 C S/O=0.0154 pH=2</td>
<td>109</td>
<td>0.1</td>
<td>3409</td>
<td>0.6</td>
<td>18.0</td>
</tr>
<tr>
<td>T=50 C S/O=0.0154 pH=2</td>
<td>108</td>
<td>0.1</td>
<td>3409</td>
<td>0.6</td>
<td>18.0</td>
</tr>
<tr>
<td>T= 60 C S/O=0.0154 pH=2</td>
<td>106</td>
<td>0.1</td>
<td>3732</td>
<td>0.6</td>
<td>12.0</td>
</tr>
<tr>
<td>T=60 C Surf=0.0154 pH=2</td>
<td>106</td>
<td>0.1</td>
<td>3634</td>
<td>0.5</td>
<td>15.4</td>
</tr>
<tr>
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<td>3586</td>
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<td>16.2</td>
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<td>3626</td>
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<td>19.5</td>
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<tr>
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<td>0.1</td>
<td>3615</td>
<td>0.6</td>
<td>15.9</td>
</tr>
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<td>3449</td>
<td>0.6</td>
<td>76.5</td>
</tr>
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<td>0.6</td>
<td>75.6</td>
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<tr>
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<td>3479</td>
<td>0.6</td>
<td>75.6</td>
</tr>
<tr>
<td>T=60 C</td>
<td>S/O=0.046</td>
<td>pH=2</td>
<td>30</td>
<td>0.1</td>
<td>3773</td>
</tr>
<tr>
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<td>-----</td>
<td>------</td>
</tr>
<tr>
<td>T= 60 C</td>
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<td>pH=2</td>
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<td>0.1</td>
<td>3779</td>
</tr>
<tr>
<td>T=60 C</td>
<td>S/O=0.046</td>
<td>pH=2</td>
<td>32</td>
<td>0.1</td>
<td>3719</td>
</tr>
<tr>
<td>T=22 C</td>
<td>S/O=0.046</td>
<td>pH=10</td>
<td>31</td>
<td>0.1</td>
<td>3660</td>
</tr>
<tr>
<td>T=22 C</td>
<td>S/O=0.046</td>
<td>pH=10</td>
<td>33</td>
<td>0.1</td>
<td>3573</td>
</tr>
<tr>
<td>T=22 C</td>
<td>S/O=0.046</td>
<td>pH=10</td>
<td>31</td>
<td>0.1</td>
<td>3660</td>
</tr>
<tr>
<td>T=60 C</td>
<td>S/O=0.046</td>
<td>pH=10</td>
<td>28</td>
<td>0.1</td>
<td>3575</td>
</tr>
<tr>
<td>T=60 C</td>
<td>S/O=0.046</td>
<td>pH=10</td>
<td>27</td>
<td>0.1</td>
<td>3544</td>
</tr>
<tr>
<td>T=60 C</td>
<td>S/O=0.046</td>
<td>pH=10</td>
<td>29</td>
<td>0.1</td>
<td>3559</td>
</tr>
</tbody>
</table>
Table 5.4 Comparison of the Online and Offline Experimental Results along with the Results Obtained for the Styrene Emulsion

<table>
<thead>
<tr>
<th>Experiment Name</th>
<th>Experiment Conditions</th>
<th>Mean diameter of small particle population</th>
<th>Std deviation of small particle population</th>
<th>Mean diameter of large particle population</th>
<th>Std deviation of large particle population</th>
<th>Wt% of decane in small particle population</th>
</tr>
</thead>
<tbody>
<tr>
<td>Online Data</td>
<td>T = 22°C Surf/Oil = 0.03 pH = 6.89</td>
<td>29</td>
<td>0.13</td>
<td>3759</td>
<td>0.58</td>
<td>70.7</td>
</tr>
<tr>
<td>Offline data</td>
<td>T = 22°C Surf/Oil = 0.03 pH = 6.89</td>
<td>32</td>
<td>0.13</td>
<td>3299</td>
<td>0.57</td>
<td>68.2</td>
</tr>
<tr>
<td>Spectrum of the Styrene in water emulsion before the reaction begins</td>
<td>T = 60°C Surf/Oil = 0.043 pH = 7</td>
<td>37</td>
<td>0.10</td>
<td>3246</td>
<td>0.20</td>
<td>36.8</td>
</tr>
</tbody>
</table>

As mentioned earlier in this section, the transmission spectrum for the styrene in water emulsion was analyzed for the wavelength region, 200 to 820nm. Excellent fit between the estimated and measured spectrum indicate that the estimates of the parameters of the droplet size distribution of each of the population comprising the emulsion are reliable. Figure 113 shows the fit between estimated and the measured spectrum.
5.3 Surfactant Stabilized Area Analysis

Analysis on the surfactant distribution over the particle populations of the dispersed phase enabled the feasibility studies for the existence of a particular particle population. In doing so, the area required to be stabilized per surfactant molecule was calculated. The following procedure was followed to calculate the area stabilized by the surfactant:

It is known from the literature that the area stabilized per molecule of surfactant for large particles is $0.48 \text{ nm}^2$. From the estimate of the particle number of the large particle population and from the estimated size distribution, the surface area of the large particles in the diluted sample present in the cuvette was calculated. Assuming representative sampling, the estimated concentration of the surfactant in the cuvette was calculated from the surfactant/oil ratio in the recipe. The number of molecules required to stabilize the large particle population were calculated by the formula:

$$N_{\text{surfmolecules}} = \frac{\text{Area of large particle population}}{\text{Area stabilized by one surfactant molecule}}$$  \hspace{1cm} (5.1)$$

$$AmS = \text{MolWt} \ast \frac{N_{\text{surfmolecules}}}{\text{Avogadro's Number}}$$  \hspace{1cm} (5.2)$$

where $AmS$ is the amount of surfactant for stabilization for large droplet population.

The remaining amount of surfactant was thought to be available for stabilizing the small particle population. The surface area of the small particle population that needs to be stabilized was calculated from the estimate of the particle number of the small particle population and from their estimated size distribution characteristics. In order to obtain the
area required to be stabilized per molecule of the surfactant for the small particle population, following calculations were performed:

Weight of surfactant required to stabilize = Total Wt of surfactant – Weight of surfactant utilized to stabilize large population

\[ N_{msmop} = \frac{\text{Emulsifier wt to stabilize small particles}}{\text{Surfactant Mol Wt}} \]  \hspace{1cm} (5.3)

where

\( N_{msmop} \) = Number of moles of surfactant required to stabilize small particle population

\( N_{msmop} = N_{msmop} \times \text{Avogadro's number} \)  \hspace{1cm} (5.4)

where

\( N_{msmop} \) = Total number of surfactant molecules required to stabilize the surface area of small particle population

Avogadro’s number = 6.022*10^{23}

Therefore,

\[ S_{stabreq} = \frac{\text{Total Surface Area of Small Particles}}{N_{msmop}} \]  \hspace{1cm} (5.5)

where

\( S_{stabreq} \) is the surface area of the small particle population required to be stabilized by one molecule of the surfactant

The results obtained from the calculations described were performed for all the cases and are expressed in Table 5.5.
Table 5.5 Comparison of the Surfactant Distribution Over Each Population of the Dispersed Phase

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>Total surface area in nm² * 10¹⁵</th>
<th>Surface Area of small particles * 10¹⁵</th>
<th>Surface Area for large particles * 10¹⁴</th>
<th>Amount of surfactant large particles in grams/ml * 10⁻⁷</th>
<th>Amount of surfactant on small particles in grams/ml * 10⁻⁶</th>
<th>Area stabilized per molecule for large particles in nm²</th>
<th>Area stabilized per molecule for small particles in nm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>T =50 deg C pH = 2 Surf/oil =0.0154</td>
<td>7.9</td>
<td>7.5</td>
<td>3.7</td>
<td>3.4</td>
<td>8.6</td>
<td>0.48</td>
<td>0.4</td>
</tr>
<tr>
<td>T =60 deg C pH = 2 Surf/oil =0.0154</td>
<td>4.3</td>
<td>4.0</td>
<td>2.3</td>
<td>2.1</td>
<td>5.4</td>
<td>0.48</td>
<td>0.35</td>
</tr>
<tr>
<td>T =60 deg C pH = 10 Surf/oil =0.0154</td>
<td>9.3</td>
<td>8.9</td>
<td>3.8</td>
<td>3.5</td>
<td>10</td>
<td>0.48</td>
<td>0.4</td>
</tr>
<tr>
<td>T =50 deg C pH = 2 Surf/oil =0.046</td>
<td>344</td>
<td>344</td>
<td>3.3</td>
<td>3.0</td>
<td>82.5</td>
<td>0.48</td>
<td>1.88</td>
</tr>
<tr>
<td>T =60 deg C pH = 2 Surf/oil =0.046</td>
<td>449</td>
<td>449</td>
<td>2.94</td>
<td>2.7</td>
<td>91.7</td>
<td>0.48</td>
<td>2.21</td>
</tr>
<tr>
<td>T =22 deg C pH = 10 Surf/oil =0.046</td>
<td>435</td>
<td>434</td>
<td>4.02</td>
<td>3.7</td>
<td>100</td>
<td>0.48</td>
<td>1.94</td>
</tr>
<tr>
<td>T =60 deg C pH = 10 Surf/oil =0.046</td>
<td>420</td>
<td>419</td>
<td>2.9</td>
<td>2.6</td>
<td>82.5</td>
<td>0.48</td>
<td>2.29</td>
</tr>
</tbody>
</table>
An interesting observation is that, for the emulsion recipe with low surfactant to oil ratio, the area stabilized per molecule of the surfactant for small particle population is in close agreement with the values reported in literature\textsuperscript{54,55}. This suggests that the diluted sample obtained inside the cuvette is stable and hence, the information drawn from these measurements are reliable and meaningful. Consistency in the results obtained for the replicate measurements and replicate samples satisfactorily address the issue of sample integrity and stability. Since the sample obtained from emulsion recipe with low surfactant/oil ratio is stable, the sample obtained from the emulsion recipe with high surfactant/oil ratio can also be inferred to be stable.

Calculations were also performed to test the probability of the existence of particle populations with size characteristics of swollen and empty micelles that could be formed by the residual surfactant after stabilizing large particle population. Since the weight of the oil phase that is dispersed in small particle population has been estimated by spectroscopy, the amount of area needed to be stabilized by each surfactant molecule to achieve the dispersion droplets of required size distribution was calculated using the following equations:

Number of small particles of the size range of swollen micelles or empty micelles is calculated by equation 5.6 (assuming that these particles are monodispersed)

\[
N_{\text{small}} = \frac{W_t \text{ of oil phase to be stabilized}}{\text{Vol of one particle} \times \text{Density}} \tag{5.6}
\]
where $N_{smpa}$ is resulting the number of particles of the size characteristics of the swollen or empty micelles for dispersing the estimated amount of oil.

Total area of small particles is given by equation 5.7 as

$$Total\ area\ of\ small\ particles = 4\pi r^2 N_{smpa}$$

(5.7)

Area required to be stabilized per particle by one surfactant molecule can be calculated by equation 5.5.

Results shown in Table 5.6 indicate that a much higher area will have to be stabilized by one surfactant molecule for the dispersed phase to be of size range of swollen micelles (5 to 10 nm diameter) than for the size range of nano-droplets (30 to 100 nm diameter) to achieve the same amount of oil dispersion. This would suggest that the probability of the presence of the swollen micelles is much lower than the presence of the nano-droplets for the given quantity of the surfactant available and the amount of oil required to be dispersed. In other words, the required quantity of surfactant to disperse the same amount of oil phase into a particle population of size characteristics of a swollen micelle or empty micelles is much higher than the quantity of surfactant available in the recipe.
Table 5.6 Comparison of the Area Required to be Stabilized per Surfactant Molecule to Achieve a Dispersed Phase of Given Size Characteristics

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Area required to be stabilized per molecule for nano-droplets</th>
<th>Area required to be stabilized per molecule for 10nm dispersed micelles</th>
<th>Area required to be stabilized per molecule for 3nm dispersed micelles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment 1</td>
<td>0.4</td>
<td>4.54</td>
<td>15.13</td>
</tr>
<tr>
<td>Experiment 2</td>
<td>0.35</td>
<td>3</td>
<td>10.00</td>
</tr>
<tr>
<td>Experiment 4</td>
<td>0.4</td>
<td>4.03</td>
<td>13.44</td>
</tr>
<tr>
<td>Experiment 5</td>
<td>1.88</td>
<td>6.18</td>
<td>20.6</td>
</tr>
<tr>
<td>Experiment 6</td>
<td>2.21</td>
<td>6.47</td>
<td>21.58</td>
</tr>
<tr>
<td>Experiment 7</td>
<td>1.94</td>
<td>6.26</td>
<td>20.88</td>
</tr>
<tr>
<td>Experiment 8</td>
<td>2.29</td>
<td>6.53</td>
<td>21.77</td>
</tr>
</tbody>
</table>

5.4 Conclusion

The above results suggest that the feasibility of the small population of the dispersed phase having the size characteristics of the nano-droplets (diameter around 30 nm) is higher than those of the swollen or empty micelles.
Figure 27 Comparison of the Experimental and Estimated Spectrum for Experiment 1

Figure 28 Comparison of the Experimental and Estimated Spectrum for Experiment 2
Figure 29 Comparison of the Experimental and Estimated Spectrum for Experiment 4

Figure 30 Comparison of the Experimental and Estimated Spectrum for Experiment 5
Figure 31 Comparison of the Experimental and Estimated Spectrum for Experiment 6

Figure 32 Comparison of the Experimental and Estimated Spectrum for Experiment 7
Figure 33 Comparison of the Experimental and Estimated Spectrum for Experiment 8
Figure 34 Comparison of the Online Experimental and the Estimated Spectra at Low Temperature

Figure 35 Comparison of the Offline Experimental and the Estimated Spectra at Low Temperature
Figure 36 Effect of pH on the Mean Diameter \( D_n \) of Nano-droplet Population at Different Conditions of Surfactant to Oil Ratio in the Emulsion Recipe. 95% Confidence Intervals are denoted by ‘+’. Continuous Lines Suggest Trend

Figure 37 Effect of pH on the Standard Deviation of Nano-droplet Population at Different Conditions of Surfactant to Oil Ratio in Emulsion Recipe. 95% Confidence Intervals are denoted by ‘+’. Continuous Lines Suggest Trend
Figure 38 Effect of pH on the Weight Percent of Oil in the Nano-droplet Population at Different Conditions of Surfactant to Oil Ratio in Emulsion Recipe. 95% Confidence Intervals are denoted by ‘+’. Continuous Lines Suggest Trend

Figure 39 Effect of Surfactant to Oil Ratio in Emulsion Recipe on the Mean Diameter Dn of the Nano-droplet Population at Different Conditions of Temperature and pH. 95% Confidence Intervals are denoted by ‘+’. Continuous Lines Suggest Trend
Figure 40 Effect of Surfactant to Oil Ratio in Emulsion Recipe on the Standard Deviation of the Nano-droplet Population at Different Conditions of Temperature and pH. 95% Confidence Intervals are denoted by ‘+’. Continuous Lines Suggest Trend

Figure 41 Effect of Surfactant to Oil Ratio in Emulsion Recipe on the Weight Percent of Oil in the Nano-droplet Population at Different Conditions of Temperature and pH. 95% Confidence Intervals are denoted by ‘+’. Continuous Lines Suggest Trend
Figure 42 Effect of Temperature on the Mean Diameter (Dn) of the Nano-droplet Population at Different Conditions of Surfactant to Oil Ratio and pH of the Emulsion Recipe. 95 % Confidence Intervals are denoted by ‘+’. Continuous Lines Suggest Trend

Figure 43 Effect of Temperature on the Standard Deviation of the Nano-droplet Population at Different Conditions of Surfactant to Oil ratio and pH of the Emulsion Recipe. 95 % Confidence Intervals are denoted by ‘+’. Continuous Lines Suggest Trend
Figure 44 Effect of Temperature on the Weight Percent of Oil in the Nano-droplet Population at Different Conditions of Surfactant to Oil Ratio and pH of the Emulsion Recipe. 95 % Confidence Intervals are denoted by ‘+’. Continuous Lines Suggest Trend
Figure 45 Effect of the Different Emulsification Conditions on the Mean Diameter $D_n$ of the Large Droplet Population

Figure 46 Effect of the Different Emulsification Conditions on the Standard Deviation of the Large Droplet Population
CHAPTER 6: CONCLUSION AND RECOMMENDED FUTURE WORK

This dissertation project has been focused on the identification of the most likely nucleation locus in emulsion polymerization processes. The preceding chapters have underscored the importance of their identification for elucidating the nucleation mechanism. Limitations associated with the experimental tools available to the past and current researchers in getting the relevant information for identifying the nucleation locus have been highlighted. The Uv vis spectroscopic techniques coupled with the algorithms developed in-house have been identified as the experimental tool for the characterization of the reaction mixture. These techniques provide the relevant and necessary information of the reaction mixture for identifying the most likely nucleation locus. The approach and the thought process using a non-reacting model emulsion system have been delineated. The hypothesis on the most likely nucleation locus has been proposed and the experimental efforts undertaken to prove it have been described. This chapter focuses on the conclusions that were based on the obtained experimental results and the calculations performed. Contributions as a result of this research work have been enumerated along with the recommendations for future work.
6.1 Conclusions

The model molecules having similar physico-chemical properties (viscosity, surface tension, vapor pressure and density) and hence the dispersion characteristics can be successfully used to mimic the actual behavior of the dispersed phase. This approach enables the characterization of the dispersed phase in terms of the size and composition. The distribution of the emulsion component of interest can be studied using appropriately labeled compound.

A nano-droplet population of size of 30 to 100 nm diameter was found to exist in emulsion along with the large particle (monomer/ oil droplet population) of size characteristic one to a few microns. These nano-droplet populations were found to contain 12 to 80% of the dispersed oil phase depending upon the emulsification conditions. High interfacial area offered by the nano-droplets and high content of oil phase in them make them a strong candidate for being the most likely nucleation locus for emulsion polymerization processes.

Total number of the nano-droplets formed, their size distribution characteristics and the weight fraction of the dispersed phase present in the nano-droplet population were found to be primarily influenced by the emulsifier concentration. pH of the suspending medium and the temperature did influence the size and the number characteristics of the nano-droplet population significantly.
The size and the number characteristics of the large droplet population remained significantly unaffected by the emulsification conditions namely, surfactant concentration, pH of the suspending medium and temperature. The nano-droplet population has a much narrower distribution (around 0.1) as compared to the large particle population (around 0.6).

6.2 Contributions

1. Identifying the existence of the nano-droplet population and characterizing them by their number and size distribution

2. Identification of the nano-droplet population as the main nucleation loci for emulsion polymerization reaction

3. Identifying surfactant to oil ratio as the process variable that predominantly governs the size, composition and the number characteristics of the nano-droplet population.

The contributions enumerated above enable a better understanding of the emulsification process. This study provides useful insight in addressing the issue of nucleation mechanisms in emulsion polymerization process by identifying a nano-droplet population as the likely nucleation loci and characterizing them in terms of their size, composition and number.
6.3 Recommendations for Future Work

The results shown in Table 5.3 indicate emulsifying efficiency per molecule of the surfactant increases with increase in surfactant concentration. Further work is recommended in this direction, since estimation of the amount of surfactant distributed over each droplet population remains an unresolved issue as yet. Obtaining a good estimate of the optical properties of emulsifier is essential for quantifying the amount of emulsifier on each of the population of the dispersed phase so that actual area stabilized by each emulsifier molecule on population of the dispersed phase can be determined experimentally. The hypothesis on emulsification efficiency as a function of emulsifier concentration can thus be addressed in future for the complete characterization of emulsion and in depth understanding of the emulsification process.

Nucleation models considering nano-droplets as the nucleation loci need to be developed and tested. Effect of the size and compositional characteristics of the nano-droplets as the likely reaction loci on the initiation mechanism needs to be explored. Subsequent changes undergone by the nano-droplets (main reaction loci) as the reaction progresses and its effect on the particle growth and propagation reaction needs to be studied.
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APPENDICES
Appendix A: Size Dependent Scattering and Absorption Particle Characteristics

In this Appendix we elaborate upon the size dependence of the scattering and the absorption components of the transmission Uv vis spectrum of a particle population as mentioned in Chapter 3. The light scattering efficiency and the absorption efficiency is dependent upon the size of the particle. Hence the shape of the transmission Uv vis spectrum for a particle population of same composition but different size characteristics is expected to be different.

![Figure 47 Schematic of the Transmission Measurement](image)

The change in the intensity of light through infinitesimally small distance ‘dl’ is given by

\[ dl = -\varepsilon_{\text{extinction}} I \, dl \]

(A-1)

where

- \( I \) is the intensity of the light
- \( dl \) is the change in the intensity of the light
- \( \varepsilon_{\text{extinction}} \) is the extinction coefficient
- \( I_0 \) is the intensity of the incident light
- \( I \) is the intensity of the transmitted light
- \( l \) is the path length

120
Appendix A: (Continued)

\[
\int_{l_0}^{l} \frac{dl}{I} = -\varepsilon_{\text{extinction}} \int_0^{l_0} dl
\]

\[
\ln \left( \frac{I}{I_0} \right) = -\varepsilon_{\text{extinction}} l
\]

\[I = I_0 e^{-\varepsilon_{\text{extinction}} l}\]  \hspace{1cm} (A-2)

\[
\varepsilon_{\text{extinction}} = \left( \frac{\pi}{4} \right) D^2 Q_{\text{extinction}}
\]

(for single particle)

Thus for a monodisperse particulate system\textsuperscript{23}

\[
I = I_0 \exp \left( -N_p \left( \frac{\pi}{4} \right) D^2 Q_{\text{extinction}} l \right) \]  \hspace{1cm} (A-3)

\[N_p = \text{number of particles per unit volume}\]

\[Q_{\text{extinction}} = \text{Extinction efficiency}\]

For a polydisperse system\textsuperscript{23,56}

\[
I = I_0 \exp \left( -N_p \left( \frac{\pi}{4} \right) l \int Q_{\text{extinction}} D^2 f(D) \ dD \right) \]  \hspace{1cm} (A-4)

\[I = I_0 e^{(-\tau(\lambda) \ l)} \]

Where \[\tau(\lambda) = N_p \left( \frac{\pi}{4} \right) l \int Q_{\text{extinction}} D^2 f(D) dD\]  \hspace{1cm} (A-5)

\[\tau (\lambda)\] is also called optical density.

Optical density is expressed as \[OD = \varepsilon_{\text{extinction}} c l\]
Appendix A: (Continued)

where \( c \) is the concentration of the dispersion

\[ c = n_p \text{ (number of particles per ml)} \]

For monodisperse system\(^{23,56}\)

\[ \epsilon_{\text{extinction}} c l = \left( \frac{\pi}{4} \right) D^2 Q_{\text{extinction}} n_p l \]

For polydisperse system

\[ \epsilon_{\text{extinction}} c l = \left( \frac{\pi}{4} \right) D^2 l \int Q_{\text{extinction}} D^2 f(D) \, dD = OD \quad (A-6) \]

where OD is the optical density

\( Q_{\text{extinction}} \) is a function of

1. Complex refractive index denoted by \( m \)

2. Size parameter denoted by \( x \)

\( Q_{\text{extinction}} \) is expressed as

\[ Q_{\text{extinction}} = Q_{\text{absorbance}} + Q_{\text{absorbance}} \]

\( Q_{\text{absorbance}} \) and \( Q_{\text{absorbance}} \) are expressed as by Bohren and Huffman\(^{56}\)

\[ Q_{\text{absorbance}} = 4 \, x \, \text{Im} \left[ \frac{m^2 - 1}{m^2 + 2} \left[ 1 + \frac{x^2 \left( \frac{m^2 - 1}{m^2 + 2} \right) m^4 + 27m^2 + 38}{2m^2 + 3} \right] \right] \quad (A-7) \]

\[ Q_{\text{scattering}} = \left( \frac{8}{3} \right) x^4 \left| \frac{m^2 - 1}{m^2 + 2} \right|^2 \quad (A-8) \]
Appendix A: (Continued)

For the small particles of size ranges much less than the wavelength of the incident light (Uv vis light), the Rayleigh scattering is the most relevant approximation. The absorption and the scattering efficiencies for Rayleigh approximations\textsuperscript{56} is given by equations A-9.

\[
Q_{\text{absorbance}} = 4 \ x \ \text{Im} \left( \frac{m^2 - 1}{m^2 + 2} \right) \left[ 1 + \frac{4}{3} \ x^3 \ \text{Im} \left( \frac{m^2 - 1}{m^2 + 2} \right) \right]
\]  
(A-9)

From the equations A-7, A-8 and A-9 it is clear that as the particle size gets smaller, its scattering efficiency decreases much more than the absorption efficiency. Hence as the particle size becomes smaller, the absorption component is expected to become more dominant while for larger particles the scattering component is expected to be more dominant in the optical density observed.
Appendix B: Spectroscopic Calculations

B.1 Introduction

This Appendix describes the preliminary calculations performed using simulated transmission Uv vis spectra that lead to the postulation of the main hypothesis in Chapter 3 of this dissertation. The calculations were performed in order to explore the possible characteristics of the Styrene in water emulsion at time zero to understand the initial conditions prevalent in the reactor prior to the beginning of the emulsion polymerization reaction. The simulation algorithms\textsuperscript{34,35} developed in-house used the turbidity equation (equation 3.1) for simulating the transmission Uv vis spectra of the styrene droplet populations having different size distribution characteristics. In this Appendix are described the calculations performed with the simulated spectra, the pertinent explanations and the inferences drawn from these studies that lead to the hypothesis postulation in Chapter 3.

The transmission Uv vis spectra were generated for a wide range of mean sizes of nano-droplet populations of Styrene ranging from 30 nm to 60 nm. The generated simulated transmission Uv vis spectra for a particle population of given size distribution and known optical properties were such that the maximum optical density was one. The corresponding concentration of the particles in the population was noted. Extinctions were obtained by dividing the spectra obtained by the respective concentrations. For large monomer droplets the extinctions were obtained in the same manner.
Appendix B: (Continued)

The spectroscopic mass balance was performed with the help of the extinctions of the small nano-droplets and large monomer droplets. The extinctions of the nano-droplets and the large monomer droplets were multiplied by appropriate fractions and then added together to obtain an extinction of the entire latex mixture of small and large particles. The shape of the extinction spectrum thus obtained is and compared with the shape of the extinction of experimentally observed spectrum of the latex mixture. The results are depicted in Figures 50 through 54.

The above explanation on spectroscopic mass balance can be expressed as

\[ E_{\text{total}} = x_{\text{small}} \times E_{\text{small}} + x_{\text{large}} \times E_{\text{large}} \]

Where

- \( x_{\text{small}} \) is the mass fraction of the small particles in the latex mixture
- \( x_{\text{large}} \) is the mass fraction of the large particles in the latex mixture
- \( E_{\text{total}} \) = total extinction
- \( E_{\text{small}} \) = extinction of small particles
- \( E_{\text{large}} \) = extinction of large particles

For the particle populations of same composition, their transmission spectrum would be a function of their size distribution characteristics alone. Therefore the relative spectral contribution of each population to the measured spectrum will be indicative of the respective concentrations of each populations. It was observed that at least 40 to 50% of the monomer is present in the small nano-droplets of the monomer ranging from sizes 30
Appendix B: (Continued)

nm to 60 nm. Since the nano-droplets are large in numbers and offer a larger surface area there is a strong possibility of they are the primary loci for nucleation. Details of the calculations performed are presented in the next section.

B.2 Sample Calculations

Spectroscopic Mass Balance:

Vector name for experimental extinction: Exexp.txt

Vector name for extinctions for big particles: Exbp.txt

Vector name for extinctions for small particles of size ‘n’ nanometers: Exn.txt

Sample calculations:

Vector for extinctions for the small particles of size 30 nm is given by:

\[ Ex_{30} = \frac{n_{30spc(:,2)}}{0.0000060536}; \]

Where

\( n_{30spc(:,2)} \) is the vector of the optical density from the simulated spectra

0.0000060536 is the concentration of the monomer in the particles.

Vector for extinctions for the big particles (monomer droplets) of size 3.2\( \mu \)m is given by:

\[ Ex_{bp} = \frac{n_{1spbp(:,2)}}{0.00012865}; \]

Where

\( n_{1spbp(:,2)} \) is the vector of the optical density from the simulated spectra obtained from the program 0.00012865 is the concentration of the monomer in the particles.

Mass balance:
Appendix B: (Continued)

Vector for extinctions for the latex mixture with small particles of size 30 nm that best fits with the experimental spectrum is given by

\[ C_{30} = 0.4 \times \text{ex}30(:,1) + 0.6 \times \text{exbp}(;1) \]

thus suggesting that 40% of total monomer is in the nano-droplet population of mean size 30 nm diameter.

The following figure compares the spectral features of the scattering component of the experimentally observed spectrum with the simulated spectrum of latex of PSD 3.2 microns as the mean diameter and 0.2 as the standard deviation.

Figure 48 Comparison for Extinction for Large Particles (Monomer Droplets Mean Size 3.2 microns Std Dev 0.2) with the Features of the Scattering Component of the Experimentally Observed Spectrum
Appendix B: (Continued)

The similarity in the spectral features of the scattering component of the experimental spectrum and the calculated transmission spectrum of the same latex with size characteristics 3.2 microns mean diameter and standard deviation of 0.2 can be noted. This indicates that the large monomer droplet population present inside the reactor at the beginning of the reaction has similar size distribution characteristics.

Figure 49 Comparison of Simulated Transmission Spectra for Particle Populations with Different Mean Sizes but the Constant Standard Deviation 0.2

From Figure 49 it is clear how the shape of the transmission spectrum of the latex changes with the size characteristics of the latex. Figures 50 through 54 show simulated extinctions of the large particle population added in proportion to the simulated extinctions of the small particle population such that they are in accordance with the
Appendix B: (Continued)

extinction of the latex obtained experimentally. The Figures 50 through 54 thus
demonstrate the results of the spectral mass balances performed. The results from the
spectral mass balances thus performed indicate that about 40 to 50 % of the monomer is
present within the nano-droplet population of mean size 30 to 60 nm in diameter.

Figure 50 Spectral Mass Balance for 30 nm and 3.2 microns Mean Diameter Population
Appendix B: (Continued)

Figure 51 Spectral Mass Balance for 40 nm and 3.2 microns Mean Diameter Population

Figure 52 Spectral Mass Balance for 45 nm and 3.2 microns Mean Diameter Population
Appendix B: (Continued)

Figure 53 Spectral Mass Balance for 50 nm and 3.2 microns Mean Diameter Population

Figure 54 Spectral Mass Balance for 60 nm and 3.2 microns Mean Diameter Population
Appendix B: (Continued)

![Graph of Particle Size Distributions with Different Mean Sizes]

Figure 55 Particle Size Distributions with Different Mean Sizes

**B.3 Inferences Drawn from the Results Obtained from the Spectral Manipulations**

From the spectral manipulations performed as described above, we conclude that the transmission spectral signal obtained at time zero can be mainly attributed to two particulate populations namely:

1. large monomer droplets (mean size 3.2 microns and standard deviation 0.2)
2. nano-droplets (mean size 30nm to 100nm in diameter and standard deviation of about 0.2)

The large monomer droplets contained around 50 to 60 percent of the monomer and the number of large particles was in the tenth order of magnitude.
Appendix B: (Continued)

The amount of monomer contained in the small nano-droplets was almost 40 to 50%.
The number of nano-droplets in the reactor was calculated to be in the order of magnitude
of about sixteen. This would be indicative of the high interfacial area that is offered by
these nano-droplets as opposed to any other particulate entity present inside the reaction
mixture in the reactor at time zero. Also the relative concentration of the monomer
content in them makes the nano-droplet population (of size range 30nm to 60nm in
diameter) the prime candidate for being the most likely nucleation loci.

Final number of the particles formed and the number of initial nano-droplets
present in the reactor before the beginning of the reaction are of the same order of
magnitude. This suggests that if nano-droplets are the main locus of nucleation then,
almost all of the nano-droplets get converted to the polymer particles. Thus governing the
characteristics of the nano-droplets by investigating the effect of initial conditions on
them is a study of practical and industrial importance.
Appendix C: Optical Properties

C.1 Introduction

This appendix describes the work undertaken to obtain the optical properties for the oil phase, continuous phase and the emulsifier. The optical properties are the inputs to the algorithms based on the turbidity equation (equation 3.1) for characterizing the dispersed phase of the emulsion in terms of the number of populations of the dispersed phase, and the number of particles, size distribution and the composition of each of the dispersed phase population.

The real and the imaginary parts of the complex refractive index known as the refractive index and absorption coefficients respectively constitute the optical properties of a compound. Optical properties of the dispersed phase, continuous phase and the emulsifier are desired in order to interpret the Uv vis spectroscopy data of the emulsions at different emulsification conditions.

The complex refractive index is expressed as

\[
m(\lambda_0) = \frac{n(\lambda_0) + ik(\lambda_0)}{n_0(\lambda_0)} \quad \text{C-1}
\]

\(n(\lambda_0)\) is the real part of the refractive index of the particles dispersed
\(k(\lambda_0)\) is the absorption coefficient of the particles dispersed
\(n_0(\lambda_0)\) is the real part of the refractive index of the suspending medium
Appendix C: (Continued)

The droplets dispersed in a liquid-liquid emulsion systems are primarily composed of dispersed phase and the emulsifier. These dispersed droplets are suspended in the continuous medium. The optical properties for all the components of the emulsion (dispersed phase, continuous phase and the emulsifier), need to be determined as a function of wavelength and for the emulsification conditions of interest. Since the scattering and absorption components are characterized by the optical properties, it is essential to have good estimates of the optical properties of to interpret the Uv vis spectroscopy data using the light scattering and absorption theories. The Uv vis spectroscopy data is interpreted in terms of particle number, particle composition and particle size distribution of the particulate populations that comprise the emulsion at different emulsification conditions using the turbidity equation based on Mie scattering theory.

The optical properties of all the compounds constituting the emulsion namely, decane (the dispersed oil phase), water (the continuous phase) and the emulsifier Sodium Dodecyl Benzene Sulfonate (referred to as SDBS henceforth) were obtained along with the Para- Toluene Sulfonic Acid (referred to as PTSA henceforth) as a model molecule for the SDBS. The next section describes in detail the procedure and the rationale followed to obtain the optical properties of the above compounds.
Appendix C: (Continued)

C.2 Characterization of the Optical Properties

C.2.1 Optical Properties for Decane (Dispersed Phase)

The Sellmeir-Drude\textsuperscript{57} equation was used to calculate the refractive index of decane. The Sellmeir-Drude equation to calculate the refractive index (n) for decane at temperature $T$ is given as:

$$n^2(T) - 1 = \frac{B(T)}{(V_0 + \phi^2) - \left(\frac{c}{\lambda}\right)^2}$$  \hspace{1cm} \text{C-2}

where $B$ is a constant for a particular substance and is expressed as

$$B(T) = K \cdot \rho(T)$$  \hspace{1cm} \text{C-3}

Where ‘$K$’ is a constant for a particular substance and ‘$\rho(T)$’ is the density of the hydrocarbon at temperature ‘$T$’. ‘$V_0$’ is the frequency of the electrons in the effects of dispersions. ‘$\lambda$’ is the wavelength and ‘$c$’ is the speed of light.

Value of $c = 3 \times 10^{17}$ (nanometers/s)

$\lambda$ was a vector from 190 to 820 nm (with an increment of 2 nm)

The values of $K$ and $V_0$ obtained using Cauchy equations and with the help of the values of the refractive index as a function of wavelength present in the literature were as follows
Appendix C: (Continued)

\[ K = 1.16978 \times 10^{31} \]
\[ V_0 = 2.9738 \times 10^{15} \]

\[ \phi = 4.7 \times 10^{14} \times (\rho_{20} - \rho_T) \quad \text{C-4} \]

\[ \Delta \rho = \rho_{20} - \rho_T \quad \text{C-5} \]

\[ \rho_{20} = \text{Density of decane at 20 deg C} \]

\[ \rho_T = \text{Density of decane at T Deg C} \]

In order to carry out the above calculations, we need an estimate of densities at different

temperatures. We calculated the densities by obtaining the molar volume of the decane at
different temperatures using the Gunn Yamada equation\textsuperscript{58}

\[ V(T) = \frac{f(T) \times V_R}{f(T^R)} \quad \text{C-6} \]

Where \( V(T) \) is the molar volume of decane hydrocarbon at temperature \( T \)

Where \( V_R \) is the molar volume of the hydrocarbon at the reference temperature 20 deg C.

\( T_R \) is the reduced temperature evaluated as\textsuperscript{58}

\[ T_R = \frac{T}{T_c} \quad \text{where } T_c \text{ is the critical temperature} \]

At temperature \( T \),

\[ f(T) = H_1 \times (1 - \omega \times H_2) \text{ at temperature } T \quad \text{C-7} \]

\[ H_1 = 0.33593 - 0.33953 \times T_R + 1.51941 \times T_R^2 - 2.02512 \times T_R^3 + 1.11422 \times T_R^4 \quad \text{C-8} \]

\[ H_2 = 0.29607 - 0.09045 \times T_R - 0.04842 \times T_R^2 \quad \text{C-9} \]
Appendix C: (Continued)

Thus at the reference temperature 20 deg C,

\[ f(T^R) = H_1^R \times (1 - \omega \times H_2^R) \]  \hspace{1cm} C-10

\[ H'^1 = 0.33593 - 0.33953 \times T'^R + 1.51941 \times T'^2_R - 2.02512 \times T'^3_R + 1.11422 \times T'^4_R \]  \hspace{1cm} C-11

\[ H'^2 = 0.29607 - 0.09045 \times T'^R - 0.04842 \times T'^2_R \]  \hspace{1cm} C-12

\( \omega \) is the acentric factor (a function of pressure).

The values for the acentric factor (\( \omega \)) can be calculated using Lee-Kesler equation\(^59\) of state given as

\[
\omega = \frac{\log P_c - 5.92714 + 6.09648 \times (\theta)^{-1} + 1.288621 \times \log(\theta) - 0.169347 \times (\theta)^6}{15.2518 + 1.56875(\theta)^{-1} - 13.4721 \times \log(\theta) + 0.43577 \times (\theta)^6} \]  \hspace{1cm} C-13

\( \text{Tr} = T/T_c \) where \( T_c \) is the critical temperature

\( T_c \) for decane = 617.5 deg K and the value of molar volume of decane at 20 deg C is \( V^R = 0.00513 \)

The density of decane at temperature \( T \) is obtained from its molar volume at that temperature from the following relationship

\[ \text{Density}(T) = \frac{\text{Mol.wt}}{V(T)} \]  \hspace{1cm} C-14

Densities of decane at different temperatures from equation C-14

\[ \rho_{22} = 0.7284 \]

\[ \rho_{50} = 0.706 \]

\[ \rho_{60} = 0.698 \]
Appendix C: (Continued)

therefore values of \( \phi \) from equation C-4 at different temperatures

\[ \phi_{22} = 7.52 \times 10^{11} \]

\[ \phi_{50} = 1.1269 \times 10^{13} \]

\[ \phi_{60} = 1.504 \times 10^{13} \]

To calculate the refractive indexes at different temperatures as a function of wavelength, we substitute the values of \( K, V_0 \) and the appropriate values of \( \phi \) and \( \rho \) for different temperatures in equation 2. The absorption coefficient at each wavelength is zero.

**C.2.2 Optical Properties for Water (Continuous Phase)**

The formulation used to calculate the refractive index of water as a function of wavelength for different temperatures was originally developed by P. Scheibener et al.\(^6^0\). In this exercise we use the modified version of the formulation as released by the International Association for the Properties of Water and Steam.\(^6^0\). The refractive index of water as a function of wavelength and temperature is expressed as equation C-15

\[
\frac{n^2 - 1}{n^2 + 2} \left\{ \frac{1}{\rho} \right\} = a_0 + a_1 \times \rho + a_2 \times T + a_3 \times \frac{\rho^2}{\lambda^2} + \frac{a_4}{\lambda^2} + \frac{a_5}{\lambda - \lambda_{\text{av}}} + \frac{a_6}{\lambda - \lambda_{\text{IR}}} + a_7 \times \rho^2
\]

C-15

The values of the coefficients as present in the release are as follows

\[ a_0 = 0.244257733 \quad a_4 = 1.5892057 \times 10^{-3} \]

\[ a_1 = 9.74634476 \times 10^{-3} \quad a_5 = 2.45934259 \times 10^{-3} \]

\[ a_2 = -3.73234996 \times 10^{-3} \quad a_6 = 0.900704920 \]
Appendix C: (Continued)

\[ a_3 = 2.68678472 \times 10^{-4} \quad a_7 = -1.66626219 \times 10^{-2} \]

\[ \bar{\lambda}_{uv} = 0.229202 \quad \bar{\lambda}_{IR} = 5.432937 \]

The values of \( \rho \), \( \bar{T} \) and \( \bar{\lambda} \) are given as

\( \rho \) = specific gravity of water at that temperature in grams/ cubic centimeter

\( \bar{T} \) = \( T / T_R \) \quad where \( T_R = 273.15 \) deg K \quad \( T \) is absolute temperature of water

\( \bar{\lambda} \) = \( \lambda / 589 \) \quad where \( \lambda \) \ wavelength in nanometers

In order to obtain the density of water at different temperatures the following correlation was used\(^{60,61}\)

\[
\rho = \left\{ 1 - \frac{(T + 288.9414)(T - 3.9865)^2}{508929.2(T + 68.12963)} \right\} \quad \text{C-16}
\]

where \( T \) is the temperature of water in Deg C

The value of \( \rho \) obtained at different temperatures from equation C-16 can be substituted in equation C-15 to obtain the refractive index of water at different temperatures as a function of wavelength. The absorption coefficient at each wavelength is zero.
Appendix C: (Continued)

C.2.3 Optical Properties for the Emulsifier Sodium Dodecyl Benzene Sulfonate (SDBS)

Unlike the decane and water, the SDBS shows strong absorption peaks. Therefore in order to obtain a complete set of optical properties for SDBS, the absorption coefficient at each wavelength needs to be estimated along with the estimation of the refractive index.

C.2.3.1 Callibration of the Refractometer

The refractometer (Bausch and Lomb, Abbe-3L, Bench Model) was calibrated using standards of known refractive index. The following relationship between the observed and the actual refractive index was obtained

\[ RI_{observed} = RI_{actual} \times 0.9956 + 0.0019 \]  

C.2.3.2 Estimation of Refractive Index for SDBS

Five solutions of SDBS in DI water with different concentrations were prepared and the refractive index was observed for each of them. The observed values of the refractive index were converted to the actual values of the refractive index by using the above calibration equation. The values reported are as follows
Appendix C: (Continued)

Table C.1 Refractive Index of SDBS Solution at Different Concentrations

<table>
<thead>
<tr>
<th>Concentration of Sodium Dodecyl Benzene Sulfonate on g/cc</th>
<th>Actual refractive index ( (n_s) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>1.3731</td>
</tr>
<tr>
<td>0.2375</td>
<td>1.3706</td>
</tr>
<tr>
<td>0.2256</td>
<td>1.3645</td>
</tr>
<tr>
<td>0.2143</td>
<td>1.3661</td>
</tr>
<tr>
<td>0.2036</td>
<td>1.364</td>
</tr>
</tbody>
</table>

A graph of \( n_s \) Vs C was plotted so as to obtain a straight line. The values of the slope and the intercept of the graph of \( n_s \) Vs C was noted.

The actual RI for SDBS was obtained by the following relationship

\[
 n_{SDBS} = \text{slope} \times \text{density of SDBS} + \text{RI}_{\text{DI water}}
\]

the value of the refractive index for SDBS was obtained as 1.5256. This value of the RI was in very close agreement with the refractive index of the sodium salts of the linear alkyl benzene sulfonic acid which was obtained to be as 1.5114\textsuperscript{62}. 
Appendix C: (Continued)

C.2.3.3 Estimation of Absorption Coefficients for SDBS

Since SDBS shows strong absorption peaks we need to estimate the absorption coefficients to completely define its optical properties. The absorption coefficients are obtained by obtaining the extinction coefficients of SDBS.

The standard procedure of obtaining the extinctions coefficients would be by acquiring a series of absorption spectra of the SDBS at different known concentrations from the Beer-Lambert’s law

\[ A(\lambda) = \varepsilon(\lambda) \cdot c \cdot l \] C-18

where
1. \( A(\lambda) \) is the absorption coefficient as function of wavelength
2. \( \varepsilon(\lambda) \) is the extinction coefficient as a function of wavelength
3. \( c \) is the concentration in g/cc
4. \( l \) is the path length (1 centimeter)

The values of extinction are calculated at different concentrations to remove any error. The absorption coefficients can then be obtained from the extinction data.

C.2.3.4 Use of the Model Molecule for Estimation of the SDBS Optical Properties

Due to the long chain attached to the para position relative to the sulfonated carbon of benzene ring, SDBS has a strong micelle forming tendencies even at low concentrations (CMC of SDBS = 8*10^{-3} M). These micelles will hence tend to scatter
Appendix C: (Continued)

light thus affecting the absorption signal of the SDBS in the smaller wavelength region. These would give us erroneous values of the extinctions and hence the absorption coefficients of the SDBS. The error in the optical properties of the SDBS could cause significant differences in the estimated of particulate properties from the Uv vis transmission spectroscopic signal and the actual particulate properties of the emulsion. This necessitates the use of a model molecule that would give the same Uv vis signal as the SDBS, had SDBS not scattered light in the lower wavelength region. Since the micelle forming tendency is primarily attributed to the long alkyl (dodecyl) chain attached to the benzene ring, considered another organic molecule having the same structure except the long chain was considered. This molecule was the para-toluene sulfonic acid (PTSA). PTSA has the smallest hydrocarbon (methyl group) attached at the para position of the carbon in the benzene ring to which the sulfonic acid group is attached. Also it showed similar Uv vis spectral features as the SDBS. The micelle-forming tendency is considerably low due to the absence of the long hydrocarbon chain. Thus the absorption signal obtained in the smaller wavelength region is considerably free from the scattering signal that would interfere the absorption signal due to the formation of micelles. We hence use PTSA as the model molecule to estimate the optical properties (absorption coefficients) for SDBS.
Appendix C: (Continued)

C.2.3.5 Obtaining the Optical Properties of PTSA

Absorption spectrum of dilute PTSA solutions were obtained at five different concentrations. The concentrations were noted. The optical density at 260 nm was plotted as a function of concentration of PTSA to ensure that we are in the concentration range of the PTSA such that the absorption at 260nm varied linearly with the concentration as predicted by the Beer Lambert’s law\(^56\).

Table C.2 Concentration of PTSA Solution

<table>
<thead>
<tr>
<th>Filename</th>
<th>Concentration in grams/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTSAW3.txt</td>
<td>9.263\times 10^{-5}</td>
</tr>
<tr>
<td>PTSAW4.txt</td>
<td>7.7198\times 10^{-5}</td>
</tr>
<tr>
<td>PTSAW5.txt</td>
<td>6.4335\times 10^{-5}</td>
</tr>
<tr>
<td>PTSAW6.txt</td>
<td>5.361\times 10^{-5}</td>
</tr>
<tr>
<td>PTSAW7.txt</td>
<td>4.4675\times 10^{-5}</td>
</tr>
</tbody>
</table>

We noticed that the Beer-Lambert’s law was being followed from the wavelength range 232nm to 820nm. But from 190 to 230 nm wavelength region, the relationship between the optical density and the concentration was not linear indicating the Beer-Lambert’s law was not being followed. Hence in order to obtain a better estimate of the extinctions for the smaller wavelength regions, we diluted the solutions even further.
Appendix C: (Continued)

Table C.3 Concentration of PTSA Solutions (further diluted)

<table>
<thead>
<tr>
<th>File name</th>
<th>Concentration in g/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTSAW6.txt</td>
<td>5.361*10^{-5}</td>
</tr>
<tr>
<td>PTSAW7.txt</td>
<td>4.4675*10^{-5}</td>
</tr>
<tr>
<td>PTSAW8.txt</td>
<td>3.722*10^{-5}</td>
</tr>
<tr>
<td>PTSAW9.txt</td>
<td>3.102*10^{-5}</td>
</tr>
<tr>
<td>PTSAW10.txt</td>
<td>2.585*10^{-5}</td>
</tr>
</tbody>
</table>

The extinctions for each wavelength range were estimated using the software developed inhouse. The complete extinction file for PTSA for the entire wavelength region was then obtained by joining together the appropriate values of extinctions for smaller wavelength region an (below 232 nm) and higher wavelength region (from 232 to 820 nm).

The PTSA is highly hygroscopic. It has a great affinity for water and as such captures moisture from the atmosphere. This could lead to having errors (overestimation) in the measured weight of PTSA and hence the concentration. These errors are however taken care of by the algorithms developed in house by weighting the error as a function of concentration and hence obtaining actual concentration of PTSA. The file containing the extinction coefficients as a function of wavelength is required to obtain the absorption
Appendix C: (Continued)

coefficients. The corresponding files for the extinction of SDBS were obtained by calculating the extinction using the molecular weight of SDBS separately.

The refractive index of PTSA was obtained in a manner similar for SDBS by measuring the refractive index of the PTSA solution at different concentrations. However as mentioned earlier PTSA being hygroscopic, there could be an overestimation of the PTSA concentration. The actual concentrations of PTSA solutions were obtained by plotting the difference of the actual RI and the reference RI of the PTSA Vs the measured concentration of the PTSA. The intercept on the x axis gave an estimate of the error in concentration of the PTSA. From this estimate of the error in concentration of PTSA solution, the actual concentration of the PTSA solutions were obtained.

The data final concentration of the PTSA in solution Vs the refractive index is depicted as follows:

Table C.4 Concentration Vs Refractive Index for PTSA Solutions

<table>
<thead>
<tr>
<th>Wt % of PTSA solution</th>
<th>Actual refractive index of the solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>69.56</td>
<td>1.4479</td>
</tr>
<tr>
<td>64.8</td>
<td>1.4384</td>
</tr>
<tr>
<td>60.3</td>
<td>1.4273</td>
</tr>
<tr>
<td>56.08</td>
<td>1.4203</td>
</tr>
<tr>
<td>52.11</td>
<td>1.4128</td>
</tr>
</tbody>
</table>
Appendix C: (Continued)

The refractive index for PTSA was obtained by the extrapolation of the above data to 100% thereby yielding the value of the refractive index of pure PTSA as 1.5092.

With the estimates of the refractive index for PTSA, SDBS and with the estimates of the extinctions for PTSA and SDBS, the optical properties for SDBS can be obtained using the Kramer’s Kronig transforms.

The Kramers Kronig transforms relate the real and the imaginary parts of the complex refractive index. They are expressed as

\[ n(\omega) = 1 + \frac{2}{\pi} \ast P \ast \int \frac{\Omega \ast \kappa(\Omega)}{\Omega^2 - \omega^2} d\Omega \quad \text{C-19} \]

\[ \kappa(\omega) = -\frac{2}{\pi} \ast \omega \ast P \ast \int \frac{n(\Omega)}{\Omega^2 - \omega^2} d\Omega \quad \text{C-20} \]

\( \omega \) is the frequency

P is the principal value of the integral.

If either of the \( n(\omega) \) or \( \kappa(\omega) \) is know, the other can be calculated.

To obtain the real part of the complex refractive index of the monomer, equation (C-19) is divided into three parts and is expressed as

\[ n(\omega) - 1 = \frac{2}{\pi} \left[ \int_0^{\omega_1} \frac{\Omega \ast \kappa(\Omega)}{\Omega^2 - \omega^2} d(\Omega) + \int_{\omega_1}^{\omega_2} \frac{\Omega \ast \kappa(\Omega)}{\Omega^2 - \omega^2} d(\Omega) + \int_{\omega_2}^{\infty} \frac{\Omega \ast \kappa(\Omega)}{\Omega^2 - \omega^2} d(\Omega) \right] \quad \text{C-20} \]

The above three integrals are numerically integrated\[^{34,35}\]

Optical properties for styrene are represented in figures 58 and 59.
Appendix C: (Continued)

Figure 56 Refractive Index of Decane at Different Temperatures
Appendix C: (Continued)

Figure 57 Refractive Index of Styrene

Figure 58 Absorbance of Styrene
Figure 59  Absorbance of Sodium Dodecyl Benzene Sulfonate

Figure 60  Refractive Index of Sodium Dodecyl Benzene Sulfonate
Appendix D: Behavior of Surfactant Micellar Solutions in Different Environments

This appendix depicts the change in the shape of the transmission UVvis spectrum of the micellar solution of Sodium Dodecyl Benzene Sulfonate as a function of temperature, pH of the suspending medium and the surfactant concentration (initial emulsification conditions). The change in the shape of the transmission spectrum is indicative of the change in the micelle forming characteristics of the surfactant under different emulsification conditions. This appendix shows the results of the measured transmission spectra as mentioned in Chapter 4 for identifying the variables constituting the initial emulsification conditions, whose effect on the characteristics of the dispersed phase of the emulsion needed to be investigated.

Figure 61 Effect of pH on Surfactant Micellar Solution of Different Concentrations at High Temperatures (60 Deg C)
Appendix D: (Continued)

Figure 62 Effect of pH on Surfactant Micellar Solution of Different Concentrations at High Temperatures (60 Deg C). Amplified Lower Wavelength Region
Figure 63 Effect of pH on Surfactant Micellar Solution of Different Concentrations at Low Temperatures (22 Deg C).

Figure 64 Effect of pH on Surfactant Micellar Solution of Different Concentrations at Low Temperatures (22 Deg C). Amplified Lower Wavelength Region.
Figure 65 Effect of pH on Surfactant Micellar Solution of Different Concentrations at Low Temperatures (22 Deg C). Amplified Higher Wavelength Region

Figure 66 Effect of Temperature on Surfactant Micellar Solution of Different Concentrations at pH 10
Appendix D: (Continued)

Figure 67 Effect of Temperature on Surfactant Micellar Solution of Different Concentrations at pH 10. Amplified Lower Wavelength Region

Normalized Optical Density vs. Wavelength (nm)

Figure 68 Effect of Temperature on Surfactant Micellar Solution of Different Concentrations at pH 10. Further Amplification of Lower Wavelength Region

Normalized Optical Density vs. Wavelength (nm)
Appendix D: (Continued)

Figure 69 Effect of Temperature on Surfactant Micellar Solution of Different Concentrations at pH 2.

Figure 70 Effect of Temperature on Surfactant Micellar Solution of Different Concentrations at pH 2. Amplification of Lower Wavelength Region
Appendix D: (Continued)

Figure 71 Effect of Temperature on Surfactant Micellar Solution of Different Concentrations at pH 2. Amplification Lower Wavelength Region

Figure 72 Effect of Temperature on Surfactant Micellar Solution of Different Concentrations at pH 2. Amplification of Higher Wavelength Region
Appendix E: Comparison of the Transmission Spectra of Emulsion Under Different Emulsification Conditions

This appendix depicts the transmission emulsion spectra obtained under different emulsification conditions. The change in the shape of the transmission emulsion spectra indicates change in the characteristics of the dispersed phase population of the emulsion as a function of initial emulsification conditions (namely surfactant concentration, temperature and the pH of the suspending medium). These measured transmission spectra of the emulsions (prepared under different emulsification conditions) were deconvoluted using the turbidity equation as mentioned in Chapter 3. The experimental procedure to obtain these spectra was described in Chapter 4. The results obtained as by deconvoluting these spectra are reported in Chapter 5.

Figure 73 Effect of Surfactant Concentration at Low pH (pH 2) and High Temperature (60 Deg C)
Appendix E: (Continued)

Figure 74 Effect of Surfactant Concentration at Low pH (pH 2) and High Temperature (60 Deg C). Amplified Lower Wavelength Region

Figure 75 Effect of Surfactant Concentration at Low pH (pH 2) and Low Temperature (50 Deg C)
Appendix E: (Continued)

Figure 76 Effect of Surfactant Concentration at Low pH (pH 2) and Low Temperature (50 Deg C). Amplified Lower Wavelength Region

Figure 77 Effect of Surfactant Concentration at High pH (pH 10) and High Temperature (60 Deg C)
Appendix E: (Continued)

Figure 78 Effect of Surfactant Concentration at High pH (pH 10) and High Temperature (60 Deg C). Amplified Lower Wavelength Region

Figure 79 Effect of pH at Low Surfactant Concentration (S/O Ratio = 0.0154) and High Temperature (60 Deg C)

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Appendix E: (Continued)

Figure 80 Effect of pH at Low Surfactant Concentration (S/O Ratio = 0.0154) High Temperature (60 Deg C). Amplified Lower Wavelength Region

Figure 81 Effect of pH at High Surfactant Concentration (S/O Ratio = 0.046) and High Temperature (60 Deg C)
Appendix E: (Continued)

Figure 82 Effect of pH at High Surfactant Concentration (S/O Ratio = 0.046) and High Temperature (60 Deg C). Amplified Lower Wavelength Region

Figure 83 Effect of Temperature at High Surfactant Concentrations (S/O ratio = 0.046) and High (pH= 10)
Figure 84 Effect of Temperature at High Surfactant Concentration (S/O Ratio = 0.046) and High pH (pH = 10)

Figure 85 Effect of Temperature at High Surfactant Concentration (S/O Ratio= 0.046) and High pH (pH = 10). Amplified Lower Wavelength Region
Appendix E: (Continued)

Figure 86 Effect of Temperature at High Surfactant Concentration (S/O Ratio = 0.046) and Low pH (pH = 2)

Figure 87 Effect of Temperature at High Surfactant Concentration (S/O Ratio = 0.046) and Low pH (pH = 2). Amplified Lower Wavelength Region
Appendix E: (Continued)

Figure 88 Effect of Temperature at Low Surfactant Concentration (S/O Ratio = 0.0154) and Low pH (pH =2)

Figure 89 Effect of Temperature at Low Surfactant Concentration (S/O Ratio =0.0154) and Low pH (pH =2). Amplified Lower Wavelength Region
Appendix F: Experimental Results for Determining the Stability of the Emulsion

In order to determine the time needed for the emulsion to achieve stability, the Uv vis transmission spectra of the emulsion was recorded over a period of time. The size distribution characteristics of the particle populations comprising the emulsions are reflected upon the shape of its Uv vis transmission spectra. Therefore a constant shape of the Uv vis transmission spectra will indicate that the emulsion has achieved stability and the characteristics of the particle size distribution of the particle populations comprising it are constant. Once the emulsion stability is achieved, meaningful analysis of the transmission spectrum of the emulsion can be performed to characterize the dispersed phase. In Chapter 5 is reported the analysis of the transmission spectra of the emulsion at different times before the stability is achieved. In this appendix, the spectral results for the experiment to determine the time required for the emulsion to achieve stability are reported.
Appendix F: (Continued)

Figure 90  Actual Offline Spectrum of Emulsion at Room Temperature at Different Times
Appendix F: (Continued)

Figure 91 Comparison of Normalized Offline Spectrum of Emulsion at Room Temperature at Different Times. Normalization from 230 to 820nm

Figure 92 Comparison of Normalized Offline Spectra of Emulsion at Room Temperature at Different Times when Stability is Achieved. Normalization from 230 to 820nm
Figure 93 Comparison of Normalized Offline and Online Spectrum after Stabilization of the Emulsion. Normalization Wavelength from 230 to 820 nm.

Figure 94 Comparison of the Offline and Online Normalized Spectra with Statistics.
Appendix F: (Continued)

Figure 95 Comparison of the Online and Offline Normalized Spectra with Statistics
Amplified Lower Wavelength Region
Appendix G: Calculated Particle Size Distribution of Small and Large Droplet Populations

In this Appendix are shown the calculated droplet size distributions of the dispersed phase of the emulsion for the experiments performed under different emulsification conditions. The particle size distributions shown in this appendix are normalized by the height. The comparison between the breadth and the mean of the distribution of the large and small nano-droplet population can hence be made. The parameters completely describing the depicted size distributions of the droplets are reported in Chapter 5. The change in the droplet size distribution of the nano-droplet population as a function of the initial emulsification conditions can be greatly appreciated.

Figure 96   Normalized Droplet Size Distribution for Experiment 1
Appendix G: (Continued)

Figure 97 Normalized Droplet Size Distribution for Experiment 2

Figure 98 Normalized Droplet Size Distribution for Experiment 4
Appendix G: (Continued)

Figure 99 Normalized Droplet Size Distribution for Experiment 5

Figure 100 Normalized Droplet Size Distribution for Experiment 6
Appendix G: (Continued)

Figure 101 Normalized Droplet Size Distribution for Experiment 7

Figure 102 Normalized Droplet Size Distribution for Experiment 8
Appendix H: Preliminary Results from the Emulsion Polymerization Reactions

As indicated in the introduction and the problem definition sections, the overall objective of the project is the elucidation of the particle nucleation mechanisms in emulsion polymerization reactions. The preliminary work leading to this dissertation was accomplished through a study of emulsion polymerizations under a variety of experimental conditions. This Appendix describes the efforts that lead to the formulation the approach followed in this dissertation. The reactor configuration, measurement strategy, and experimental conditions used for this study are described in this Appendix. Relevant results are presented and discussed. The experiments described in this Appendix were jointly performed. Vara\textsuperscript{21} reports the results of the non-spectroscopic measurements. The results from the spectroscopic measurements that served as the preliminary work for formulating the approach described in this dissertation are reported in this Appendix.

In this section is described the sensor array developed in the Polymer Synthesis and Characterization laboratory, USF for monitoring the emulsion polymerization reaction to understand the nucleation mechanism. The entire experimental set up, reactor configuration and the procedure in which the reaction was conducted is described.

H.1 Materials and Methods

Purified styrene was used as the monomer in this study. Water was the suspending medium. Sodium Lauryl Sulfonate was the emulsifier used. Potassium persulphate was used as the initiator. Argon gas was used to maintain inert environment. In order to carry
Appendix H: (Continued)

out the reaction, the above mentioned reactants were added in the proportions as per the
recipe in Table H.1. The experimental conditions for carrying out the reaction are listed.

Table H.1 Recipe and Experimental conditions for the Emulsion Polymerization
Reactions

<table>
<thead>
<tr>
<th>Components</th>
<th>Vendor</th>
<th>Quantities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanopure disuntiled water</td>
<td>-</td>
<td>662 grams</td>
</tr>
<tr>
<td>Styrene</td>
<td>Alderich Chemical Co.</td>
<td>228 grams</td>
</tr>
<tr>
<td>Sodium Lauryl Sulfate</td>
<td>Sigma Chemical Co.</td>
<td>10 grams</td>
</tr>
<tr>
<td>Sodium bi Carbonate</td>
<td>J. T. Baker Chemical Co.</td>
<td>1.0 grams</td>
</tr>
<tr>
<td>Potassium persulfate</td>
<td>Sigma Chemical Co.</td>
<td>1.0 grams</td>
</tr>
<tr>
<td>Temperature</td>
<td>-</td>
<td>60 Deg C</td>
</tr>
<tr>
<td>RPM</td>
<td>-</td>
<td>300</td>
</tr>
</tbody>
</table>

The emulsion polymerization latex characteristics such as density, interfacial tension and
transmission Uv vis spectrum at different times were monitored with the help of the
sensor array for understanding the nucleation mechanism as described in the later part of
this Appendix.

H.2 Experimental Setup and Reactor Configuration

Batch emulsion polymerization reactions were conducted in a one liter jacketed
glass reactor manufactured by Kontes, Glass Co. Table H.1 gives a typical the recipe
used for carrying out emulsion polymerization reactions for styrene. Since the reaction is
a thermally initiated exothermic reaction it is necessary to have an efficient
Appendix H: (Continued)

temperature control system to control the rate of the reaction. Water of appropriate
temperature is circulated through the jacket of the reactor to control the temperature of
the reaction mixture inside the reactor. The reaction mixture is drawn from the bottom of
the reactor.

Access to the contents inside the reactor throughout the reaction for monitoring
purposes is possible through the several ports of the reactor top. Through the center most
port of the reactor top, passes the stirrer that maintains constant agitation inside the
reaction mixture throughout the reaction process. The stirrer used, is a three bladed stirrer
coated with teflon tape rotating at a speed of about 300 rpm. Through the other port of the
reactor top, the thermocouples recording the temperature inside the reaction mixture are
inserted. The condenser, a jacketed tube for condensing the vapors that may be escaping
from the reactor is attached to the reactor top through a specially provided port. The two
metallic probes of the surface tensiometer monitor the interfacial tension of the reaction
mixture as function of time. A baffle is introduced from a port very close to the surface
tensiometer probes to protect the nitrogen bubbles from bursting. To prevent the
stopping of the reaction by the oxygen from the air, typically a blanket of argon is
maintained over the entire reaction mixture throughout the reaction. A slip-stream is
taken from the bottom of the reactor to the densitometer for conversion measurements.
The latex mixture coming out of the densitometer is returned to the reactor for most part.
Some of it is passed on to the dilution system where the
Appendix H:(Continued)

reaction mixture is diluted for spectrophotometric measurements. Figures 103 and 104 show the schematic of the experimental setup of the densitometer and the surface tensiometer employed in the sensor array.

H.3 Experimental Procedure

After setting up the reactor and the measurement system, the ingredients were added in the following sequence. The water is added first in the reactor, to which is then added the surfactant. The mixture is kept under constant agitation as we add monomer to it. A blanket of argon is maintained over the reaction mixture by bubbling argon through the hollow probes of the surface tensiometer continuously. A three-way valve helps to change the gas flow in the hollow probes of the surface tensiometer from Argon to Nitrogen whenever a measurement of interfacial tension is desired. The temperature of the reaction mixture in the reactor is maintained at 60 Deg Celsius by circulating hot water from the water bath in the jacket of the reactor.

Once the emulsion is stabilized, and the desired temperature for the experiment is reached, the potassium persulphate was added as the initiator. The polymerization reaction begins with the addition of the initiator. Different parameters characterizing the reaction latex such as conversion, interfacial tension and the transmission Uv vis spectrum are monitored with the help of the sensor array described below.
Appendix H: (Continued)

H.4 Sensor Array to Monitor the Emulsion Polymerization Reaction

The sensor array developed at USF laboratory consists of densitometer that gives an online estimate of the conversion throughout the reaction, surface tensiometer for measuring the interfacial tension of the reaction latex mixture and the dilution system with spectroscopic sensor for obtaining the Uv vis transmission spectrum of the reaction latex mixture.

The densitometer has a vibrating hollow U tube, the frequency of the vibration changes with the change in the density of the fluid inside it. As the conversion of the monomer to polymer increases, the density of the latex mixture in the reactor also changes thereby causing a change in the frequency of the vibration. This change in frequency of the vibration is then expressed in terms of conversion$^{21}$. Information on conversion was obtained using densitometer and validated using traditional gravimetric techniques.

Experimental data on the conversion of the monomer to polymer with respect to time is necessary for providing the information regarding the composition of the particles in homo-polymerization. Composition of the reaction site has an effect on the rate of entry of radicals and hence on the process dynamics in general. Monitoring of the conversion of the polymerization reaction, continuously and in real time is necessary to understand the thermodynamics and the kinetics of the emulsion polymerization
Appendix H: (Continued)

processes. Since the conversion is dependent upon the rate of the reaction, which in turn
depends upon the number of particles, therefore the information on conversion thus
reflects upon the number of particles formed by nucleation.

The online surface tensiometer used to obtain estimates of the interfacial tension
is a differential bubble tensiometer. It consists of two hollow probes of unequal diameter
through which is bubbled the nitrogen gas. The difference in the pressure inside the
bubbles from the respective probes is a function of the interfacial tension of the latex
mixture\textsuperscript{21}.

Experimental data on the change in surface tension of the emulsion in the reactor
with respect to time provides us with the information on the free emulsifier
concentration. The free emulsifier concentration keeps changing causing the surface
tension of the latex particulate system to go high as the reaction progresses indicating
more and more surfactant is being used up to stabilize the growing particles. The change
in the interfacial tension is indicative of the change in the emulsifier distribution. The
knowledge of the emulsifier distribution as a function of particle size and composition
will provide an insight of the colloidal chemistry and the thermodynamics of the process
to understand the nucleation mechanism.
Appendix H: (Continued)

The online Uv vis spectrum is obtained with the help of the continuous sampling and parallel dilution system developed at USF (patent number 5,907,108, (1998)). The dilution system enables the acquisition of the transmission Uv vis spectrum of the reaction latex mixture continuously and in real time. The spectrometer employed for acquiring the Uv vis spectrum was a HP 8452A spectrometer. The total time required in diluting the concentrated reaction latex mixture and acquiring its Uv vis spectrum is less than a minute in which dilution to the fifth order of magnitude was achieved. The above mentioned sensor array has been described in great detail in the works of Paul Sacoto\textsuperscript{33} and Jaime Vara\textsuperscript{21}.

Change in the shape of the transmission Uv vis spectrum of the emulsion latex provides the information on composition of the latex and the particle size distribution of that particulate system. Information on the particle size distribution is obtained by deconvoluting the transmission Uv vis spectra\textsuperscript{34,35}. Information on the early particle size distribution especially prior to the beginning of the reaction is critical in the identification of the likely nucleation loci. The information on composition can be obtained spectroscopically. Monitoring of the particle size distribution, particle number and the particle composition of all the particle population comprising the reaction mixture is possible throughout the reaction using Uv vis spectroscopic techniques. The process of emulsion polymerization can thus be better understood with the information thus obtained.
Appendix H: (Continued)

H.5 Results Obtained From the Polymerization Reaction

Different researchers have tried to extrapolate the critical information characterizing the reaction mixture during the first stage of the reaction to time zero has been the proposed approach for elucidating the nucleation mechanism. However measurements to characterize the “time zero condition” were not performed by them. This led to the development of the sensor array described earlier for monitoring the critical parameters of the emulsion polymerization reaction. However, the difficulty in sampling the reaction latex at time zero (time zero was marked by the addition of the initiator) presents the prime hurdle for understanding the nucleation mechanism. It was for this reason that the experiments were performed with the model system as described in the main body of this dissertation for studying the nucleation mechanism.

Even so, the information obtained using this sensor array provides insight into the process kinetics and thermodynamics of the emulsion polymerization process. Jaime Vara\textsuperscript{21} presents the results obtained by densitometry and the surface- tensiometer measurements for the polymerization reactions of styrene, butyl methacrylate and the copolymerization of styrene and butyl methacrylate. Vara\textsuperscript{21} reported the conversion and the change in the interfacial tension of the reaction latex as a function of time as the reaction progressed. The interfacial tension did not change much during the first stage of the reaction indicating the adsorption of only the free emulsifier on the droplet populations. The corresponding composition of the particles could be potentially obtained from the conversion estimates.
Appendix H: (Continued)

The information on the particle composition, number and populations can be obtained from the spectroscopic measurements. The change in the composition and the particle size distribution of the populations present in the reactor is reflected upon its transmission Uv vis spectrum as the reaction progresses in time. This change in the shape of the spectrum of the reaction mixture, as the reaction progresses is depicted in Figure 109. Note the decrease in the characteristic monomer peak at around 220 to 230 nm wavelength as the reaction progresses. With proper calibration, the information on the conversion of the monomer in the reaction latex can be obtained. The results are depicted in Figure 110. Information on the droplet populations, at the beginning of the reaction (before the addition of the initiator at time t=0 and 0% conversion) was obtained by deconvoluting the spectral signal. The results are presented in Table 5.4.

Strong characteristic monomer peak in the region of interest of the Uv vis spectrum makes it impossible to identify the surfactant signal. Hence the study of the surfactant distribution over the particle populations present in the dispersed phase becomes a very difficult task. The information of the surfactant distribution over the dispersed phase at the beginning of the reaction is critical for elucidating the nucleation mechanism in emulsion polymerization. This difficulty posed by the monomer emulsion systems can be overcome by the usage of the model emulsion systems showing the same dispersion characteristics but at the same time also offering a good contrast for
Appendix H: (Continued)

spectroscopy measurements. The model emulsion systems and the experiments
performed with them are described in the main body of the dissertation.

The information on the particle size distribution of the polystyrene latex present
inside the reactor after 100% conversion is presented in Table H.2. This information was
obtained by deconvoluting the entire Uv vis transmission spectrum of the polystyrene
latex obtained as a result of the polymerization reaction of styrene to polystyrene. The
particle size distribution of the final latex is represented in Figure 111.

Table H.2 Preliminary Results obtained by the deconvoluting the spectral signal obtained
at the end of the reaction (for 100% conversion)\textsuperscript{52}

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Estimates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number Average Diameter</td>
<td>87.4 nm</td>
</tr>
<tr>
<td>Standard Deviation of the Particle Size</td>
<td>1.34 nm</td>
</tr>
<tr>
<td>Distribution</td>
<td></td>
</tr>
<tr>
<td>Particle Number (Number/ml)</td>
<td>$6.0435\times10^{10}$</td>
</tr>
<tr>
<td>Residual Sum of Squares</td>
<td>$3.6\times10^{-4}$</td>
</tr>
<tr>
<td>Standard Deviation of the residuals</td>
<td>0.0012</td>
</tr>
</tbody>
</table>

H.6 Temperature Control System

The sensing element of this temperature control system is a J type thermocouple
coated with teflon tape. It remains immersed inside the reactor containing the reaction
mixture throughout the reaction. The thermocouple sends the voltage signal (analog
Appendix H: (Continued)

signals) to the A/D converter inside the computer via multiplexer. Corrective signals are sent to the final control element by the temperature control program such that the temperature inside the reactor is maintained at a desired set point. The final temperature of the flow-stream entering the reactor jacket dictates the effectiveness of the temperature control action. The temperature of this stream is governed by the valve position of the pneumatically operated control valve (the final control element). The flow diagrams of the analog and digital signals from the sensing element to the controller and from the controller to the final control element for the desired control action are shown in figure 105. Figure 106 represents the schematic of the flow path of the water for the temperature control system.
Appendix H: (Continued)

Figure 103 Schematic of Densitometer Setup
Figure 104 Surface Tensiometer Setup (Schematic)
Appendix H: (Continued)

Figure 105 Signal Flow-path for the Temperature Control System
Figure 106 Water Flow for the Temperature Control System
Appendix H: (Continued)

Figure 107 Schematic of the Dilution System (As represented by Sacoto\textsuperscript{33})

\[ C_s(n+1) = \frac{C_s(n) q_s(n)}{q_s(n) + q_d(n)} \]
Figure 108 Reactor Setup for the Polymerization Reaction with the Dilution System
Appendix H: (Continued)

Figure 109 Change in the Shape of the Transmission Spectra of the Reaction Mixture as the Reaction Progresses
Appendix H: (Continued)

Figure 110 Estimated Conversion of Styrene to Polystyrene Using Spectroscopy
Appendix H: (Continued)

Figure 111 Particle Size Distribution of the Polystyrene Particles Formed as a Result of the Polymerization Reaction After the Reaction is Completed
Figure 112 Comparison Between the Estimated and the Measured Spectra of the Styrene Emulsion at Time Zero (Before the beginning of the Reaction)
Appendix I: Protocol for Operating the Dilution System

As mentioned in Chapter 4, this appendix enumerates the steps for operating the dilution system for obtaining the transmission UV Vis spectrum of the emulsion so that it can be characterized in terms of the size and the compositional characteristics of the droplet population/s comprising it.

1. Make the decision on the type of spectrometer to be used

   The options available were a. Hewlett Packard (Model HP 8452A)
   
   b. Ocean Optics (Model S2000, PC 2000)

* Incase of an Ocean Optics Spectrometer, please follow the configuration procedure mentioned in 12 and 13 and the experimental procedure from 14 through 26.

   The connections of the dilution system as elaborated in step 3 are needed to be made regardless.

2. If we are using the Hp8452A spectrometer then make sure that the spectrometer is “On” for at least 45 minutes prior to starting the experiment.

3. Make the connections of the dilution system as follows:

   a. The hose whose one end is connected to the dilution branch and the other end is immersed in the diluent tank is fit into the cartridge of the diluent pump for pumping the diluent in that branch.

   The diluent is similarly pumped into each branch of the dilution system.
Appendix I: (Continued)

The hoses of size L/S 17 (Masterflex Cole Parmer) are used for pumping the diluent in the dilution branches. These hoses fit into each of these cartridges and then locked on the pump head with 4 rollers.

Make sure that the side locks are pulled down so that the hoses are secured in place and do not change their positions even as the roller rotates. The diluent hoses communicate with the diluent tank and the dilution system.

b. The other ends of all the branches of the dilution system come together at a common meeting point leading to the “flow-through” cuvette. The other end of the “flow-through” cuvette is connected to the sink.

c. For pumping the diluted sample from one branch is pumped into another branch for further dilution, the diluted sample lines communicate from one branch of the dilution system to the other through another cartridge pump on which fit the smaller cartridges.

The L/S 13 (Masterflex Cole Parmer) hoses are placed in the smaller cartridge. These cartridges are now locked on the pump-head with 8 rollers.

Make sure that the side locks are pulled down so that the hoses are secured in place and do not change their positions as the rollers move.

d. The concentrated sample that is desired to be diluted is pumped into the first branch of the dilution system with the help of another sample pump. The sample is pumped by the manostat pump into the first branch of the
Appendix I: (Continued)

dilution system through the port provided.

Make sure that this hose is secured tightly in place by securing it with the locks.

Note: For the schematic of the dilution system refer figure 124 in Appendix I of this dissertation. Figure 125 shows the photograph of the dilution system along with the reactor assembly.

4. After giving enough time for the Hp8452 to warm up go to the Hp8452 menu and hit “scan blank”

5. The flow-through cuvette is now placed in the spectrometer cuvette holder.

6. The Diluent pump and the diluted sample pump is now turned on so that only the Diluent passes through the flow cell. Make sure that the diluent flow in the dilution system is continuous and without any air bubbles.

7. The reference is now taken.

8. The sample pump is now turned on so that the sample now enters the dilution system.

9. Appropriate positions of the valve are maintained as per the need of the stage of the dilution is required such that the spectrum obtained is within the linear range of the spectrometer.

10. As the diluted sample shows up in the flow cell another spectrum is taken.

11. The reference spectrum is subtracted from the above spectrum.

The spectrum of the sample is thus obtained.

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Appendix I: (Continued)

12. If we are using an Ocean Optics spectrometer we first need to configure it.

13. Two types of spectrometers are available depending upon whether we are using
a laptop or a desk top.

* Spectrometer Configuration for a desktop computer.

Two types of spectrometer are available for desktop usage.

1. S2000 which is a stand alone spectrometer
2. PC2000 which is a plug in spectrometer.

Procedure:

a. Shut down the computer

b. Select the Base address and the IRQ settings by changing the
appropriate switches provided on the A/D card for the S2000
spectrometer and in case of PC 2000 we select the switches provided
on the card that carries the spectrometer.

For the selection of the switches refer to “Operating Manual and User’s
guide” provided by Ocean Optics.

c. The Base address and the IRQ settings selected should not coincide
with the other devices inside the computer.

d. Now place this hardware inside the slot provided in the computer.

e. Now turn on the computer.

f. Connect the light source to the spectrometer using the optic fiber.

g. Go to Programs----OOIBase32------Spectrometer ------configure.
Appendix I: (Continued)

h. Input the serial #, Spectrometer type, A/D card type
i. Go to A/D interface and put in the value of the Base Address and the
   IRQ.
   a. Check for the signal. If we until are unable to find any signal
      then Restart the computer.

* Spectrometer Configuration for Laptop computer
  a. Spectrometer S2000 is connected to the A/D card DAQ700.
  b. This card is inserted in the laptop in the space provided.
  c. Go to Programs --------OOIBase32 ------Spectrometer----Configure.
  d. Put in the spectrometer type and serial # and the type of interface
  e. Connect the light source to the spectrometer.
  f. Restart the laptop.
  g. The spectrometer should now be configured.

14. The Flow cell is placed in the Cuvette holder from the Ocean Optics.

15. A Split fiber of 400 microns solarization proof is employed to carry the light
    from the source to the cuvette holder carrying the flowcell.
    One collecting arm of the fiber is connected to the UV source while the other
    arm is connected to the visible light source. The common arm which now
    carries both the UV and the visible light goes to the cuvette holder.

16. One 400 micron straight fiber is connected to the spectrometer which collects
    the UV Vis light coming from the flow cell and takes it to the spectrometer.
Appendix I: (Continued)

17. Note that in the Scope Mode of the OOIBase32 software the signal obtained should be between 2500 to 3000 counts.

18. We can manipulate the signal obtained by playing with the windows of the source or by manipulating the integration time.

19. The Diluent pump and the diluted sample pump is now started such that only diluent passes through the dilution system and the flow-through cuvette.

20. The “lighted yellow bulb” icon on the OOIBase32 window is hit. This is the Reference.

21. The path of the light in between the collecting fiber and the delivery fiber is completely blocked and the signal goes to zero.

22. The “dark bulb icon” on the OOIBase32 is now hit. This is the dark

23. The light path is now unblocked and the icon “A” for absorbance is now hit so that now we are in absorbance mode.

24. The sample pump is now started and the material shows up in the spectrum in absorbance mode.

25. Care should be taken in maintaining the flowrate of the pumps so that we obtain absorbance within the linear range of the spectrometer.

26. The sample spectrum is saved by:

File----save experiment----giving the filename----and hitting save.
ABOUT THE AUTHOR

Vineet Shastry completed his Bachelor’s degree in Chemical Engineering from the University of Mumbai (Bombay), India in 1996. Vineet Shastry, as an undergraduate worked on the techno-economic feasibility of portable desalination plant to solve the problem of drinking water in his district (county) in India. After completing his undergraduate course work in Chemical Engineering, he worked as a trainee Chemical Engineer in the Sulfuric Acid Plant of M/s Albright and Wilson Chemicals, (India) Ltd. This industrial experience motivated him to pursue his graduate studies. Vineet Shastry started working on his Ph.D. degree in Chemical Engineering at the University of South Florida, Tampa Florida, USA under the guidance of Prof. Dr L H Garcia-Rubio in 1998.