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Light scattering study of attractive interactions in a model microemulsion system

Dawn M. Campbell

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LIGHT SCATTERING STUDY OF ATTRACTIVE INTERACTIONS IN A MODEL MICROEMULSION SYSTEM

by

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Submitted to the Center for Materials Science and Engineering, Rochester Institute of Technology, Rochester, New York 14623

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

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LIGHT SCATTERING STUDY OF ATTRACTIVE INTERACTIONS IN A MODEL MICROEMULSION SYSTEM

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LIGHT SCATTERING STUDY OF ATTRACTIVE INTERACTIONS IN A MODEL MICROEMULSION SYSTEM

Dawn M. Campbell

Center for Materials Science and Engineering, Rochester Institute of Technology, Rochester, New York 14623

Abstract

Static and dynamic (photon correlation spectroscopy) light scattering studies were conducted on AOT/WATER/n-DECANE microemulsions near room temperature. The molar ratio of water to AOT was varied from W = 20 to 30. The volume fractions of the studied microemulsions ranged from $\Phi = 0.03$ to 0.45. Static light scattering data was modeled by a theory based on attractive perturbations to hard spheres. From the model, values for $A$, the attractive perturbation to the second virial coefficient, were determined. It was found that $A$ is an increasing function of $W$. Photon correlation spectra were analyzed in terms of an adhesive sphere model to produce corresponding values of $A$, which were compared to the statically determined $A$-values. The two methods produced $A$ values that were not in agreement within experimental error, however the methods independently had reasonable agreement between theory and experiment.
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Chapter 1. INTRODUCTION

1.1 Introduction to the field

There have been previous studies on colloidal systems that predict the basic interaction potential due to interparticle forces. Micellar and microemulsion suspensions have been appropriate systems for these studies.\textsuperscript{1,2,3,4,5,6} Current belief is that microemulsions which contain reversed swollen micelles have a strong short range attractive force due to the interpenetration of the surfactant tails residing on the surface of the interacting particles.\textsuperscript{4} The AOT/Water/n-Decane microemulsion system is considered to be a model system because it achieves thermodynamic stability with only three components near room temperature. This microemulsion system has been studied using various techniques including small angle neutron scattering (SANS)\textsuperscript{3}, small angle x-ray scattering (SAXS)\textsuperscript{6} and light scattering\textsuperscript{4}, to name a few. The present study employs static light scattering and photon correlation spectroscopy (PCS), also called dynamic light scattering (DLS), to study the interaction between particles in the AOT/H\textsubscript{2}O/n-DECANE microemulsion system.
Light scattering is a particularly appealing way to study microemulsion systems because it is non-destructive and requires small sample volumes (approximately 3 ml). The following section briefly discusses colloidal systems. Then the subgroup of microemulsions, and micellar microemulsions, in particular, are discussed.

COLLOIDAL SYSTEMS:

"A colloidal system consists of a finely dispersed phase (or discontinuous phase) distributed uniformly in a finely divided state in a dispersion medium (or continuous phase)."7 There are colloidal systems all around us, for instance, fog is a discontinuous water droplet phase in a continuous air phase and milk is a discontinuous fat droplet phase in a continuous aqueous phase. The dispersed phase in these colloidal systems usually has dimensions in the range of 1 - 1000 nm, and is finely divided throughout the continuous phase. In some colloidal systems, however, the dispersed phase particles are much larger than 1000 nm, hence the limits given above are not rigid.7
One type of a colloidal system is an emulsion. An emulsion consists of a fluid dispersed phase in a fluid dispersion medium. In most instances, emulsions either consist of aqueous droplets in oil, a water-in-oil (W/O) emulsion, or an oil-in-water (O/W) emulsion. Milk is an example of a O/W emulsion with fat droplets in an aqueous medium whereas mayonnaise is an example of an W/O emulsion with aqueous droplets in an oil medium.

One factor that determines whether or not an O/W or W/O emulsion forms is the ratio of the amounts of the two phases present (the ratio of the phase volumes). In most cases the dispersed phase is the phase which is present in the lower amount. When an emulsion forms, there is an increase in free energy in the system as well as an increase in interfacial area between the two phases present. The amount of work required for the emulsion formation is determined by the interfacial tension. As the interfacial tension decreases, so does the amount of work needed to form the emulsion, so emulsions form more readily as the interfacial tension decreases. In addition, the attainable droplet size decreases as the interfacial tension decreases. In fact, if the interfacial tension of a system approaches zero, spontaneous emulsification may occur. The droplet size
in these spontaneously formed systems is very small (< 10 nm diameter) and so the droplets scatter little light which makes the dispersions clear. These systems that are formed spontaneously are called microemulsions, they consist of at least three components (e.g., oil, water and surfactant) and are thermodynamically stable. Some microemulsions need a fourth component (cosurfactant) in order to achieve stability. One of the major driving forces for the intense study of microemulsions in recent years is their possible use in tertiary oil recovery. In addition there is a general academic interest in learning about the particle interactions in complex fluid systems.

The microemulsion structure may be that of random or very ordered lamellar sheets, bicontinuous, or micellar, to name a few. The experimental system chosen in the present study was a micellar microemulsion, hence the following text will give a brief introduction to the structure and types of micelles.

A micelle can be formed with water and a surface active molecule (surfactant). The surfactant is an amphiphile which means it is a molecule consisting of two parts, "one portion is a hydrophobic hydrocarbon chain (or tail); the other is a hydrophilic polar head. The
existence of these opposing properties in the same molecule, when dissolved in a solvent, is the origin of the thermodynamic driving force for micellar formation.8 For instance, when a surfactant, which has this polar head group, is added to water it maximizes the polar head groups contact with water and minimizes the non-polar tail groups contact with the water. See Figure 1.1 for the structure of a micelle consisting of surfactant in water.

FIGURE 1.1: MICELLE (in water), actually a 3-D sphere8

On the other hand, if the surfactant is added to a hydrocarbon fluid (oil), the lower free energy state is obtained when the tail groups have maximum contact with the hydrocarbon fluid and the polar head groups minimize their contact with the hydrocarbon fluid. In this case it
is called a reversed micelle. This structure is shown in the following figure.

![Diagram of a reversed micelle](image)

FIGURE 1.2: REVERSED MICELLE (in hydrocarbon fluid), actually a 3-D sphere

Not only are there micelles and reversed micelles, there are swollen micelles and reversed swollen micelles. A swollen micelle can be formed if another component is added to the system. For example, by adding a small amount of oil to the micelle in water system, a swollen micelle is formed. Whether it is a swollen micelle or a reversed swollen micelle is generally dependent upon the volume fractions of the components in the system. For instance, if a small amount of oil is added to the micelle in water system, the oil situates itself such that it has maximum contact with the non-polar tail groups, and the surfactant keeps its polar head groups in
maximum contact with the water. See Figure 1.3 for the swollen micelle structure.

FIGURE 1.3: SWOLLEN MICELLE, actually a 3-D sphere

Likewise, if a small amount of water is added to the reversed micelle in hydrocarbon fluid system, the water pools up in the center of the surfactant molecules due to steric and electrostatic repulsive forces of the polar heads as well as the hydrophobic effect. This is called a reversed swollen micelle, as shown in Figure 1.4.
FIGURE 1.4: REVERSED SWOLLEN MICELLE, actually a 3-D sphere\textsuperscript{18}
1.2: Problem and Method

The adhesive hard sphere model has been shown to accurately describe the short range attractive interaction observed in some colloidal suspensions. Microemulsions comprising of AOT, water and oil have been shown to exhibit a short range interaction potential due to the overlapping of the surfactant tails. The effect of changing the micelle dimension on the strength of this interaction has not been previously examined in detail.

The present study employs a model that assumes an attractive interaction between particles to analyze the static light scattering data. Photon correlation spectroscopy data is analyzed using the adhesive sphere model. This adhesive sphere model has previously been applied to the AOT/Water/Oil microemulsion system in SAXS studies. A major finding in these studies is that the interaction potential changes with the droplet concentration. In fact, the stickiness was found to decrease significantly with increasing water volume fraction. In the present study, the relationship between the attractive interaction potential and the
water to AOT molar ratio, which is related to the size of the micelles, is examined.
Chapter 2. LIGHT SCATTERING TECHNIQUES

2.1 Essentials of Instrument Setup:

A model SP127-35 35 mW Helium-Neon laser with wavelength = 632.8 nm was used with a Brookhaven Instruments BI-200SM Goniometer version 2.0. The goniometer houses a high quality glass vat in which there is decahydroneaphthalene (decalin), an index matching fluid. The decalin was supplied by Aldrich Chemical Co. Inc. with > 99% purity. In the center of the vat is a holder for a 12 mm nominal diameter round sample cell. An EMI-9863 photomultiplier tube (PMT) with a reported dark count of 20 counts/sec was used to detect the scattered light. The PMT is powered by a 0 - 3000 volt EG&G ORTEC high voltage power supply set at 2050 volts. The signal is then sent to a BI-2030AT Digital Correlator, with 136 real time data channels and 6 real time delay channels, and a BI computer for processing. The index matching fluid and the samples are kept at constant temperature using a Fisher Scientific Isotemp Refrigerated circulator Model 9000 with 0.1°C accuracy. In addition, a BI filtration system was used for filtering the index matching fluid in the vat. See Figure 2.1 for an illustration of the components.
FIGURE 2.1: EXPERIMENTAL SETUP USED FOR STATIC LIGHT SCATTERING AND PHOTON CORRELATION SPECTROSCOPY STUDIES.

The alignment of the system should be checked periodically. At the beginning of the present study the
alignment was checked at least once a month, when no significant variances were observed at the scattering angle of 90°, the alignment was checked approximately once every three months. Also, in the summer months when the weather proves to be increasingly detrimental, the alignment was checked more frequently, on the order of once or twice a week. The procedure for checking the alignment is outlined in the Light scattering manual provided by Brookhaven Instruments Corporation, in the alignment section, page 7-4 through 7-8. It should be noted that at 90° no significant effects were observed when the sample cell was positioned so that a scratch was in the region where the beam enters the cell as opposed to a region where there were no scratches (no bright spots observed) on the sample cell. It is believed that scratches on the sample cell will have an effect on experimental results if the experiment employs small scattering angles.

The index matching fluid (decalin) has an index of refraction that is approximately equal to that of the glass vat and the glass sample cell. The purpose of this fluid is to keep the incoming laser beam from scattering when it encounters the vat-liquid and liquid-sample cell interfaces. The decalin used throughout the nine month
experimental period was the original fluid put in the system. The decalin was filtered approximately once a month for the first four months then once every four months thereafter. Filtering the decalin reduces the amount of impurities in the system however it introduces bubbles. This presents a problem as decalin is a rather viscous fluid and it was found that it took at least one week for the bubbles to either settle on the floor of the vat or rise to the surface where they would not be in the path of the beam (heating the fluid in the vat using the temperature controller accelerates the elimination of bubbles to a certain degree). Thus the index matching fluid was only filtered when it was absolutely necessary.

It is the opinion of this student that the decalin should be replaced no less than once a year. This procedure should be done with all appropriate protective equipment and in the company of another in case of an accident.

The temperature was kept constant at 23.1°C and the PMT was positioned at 90° for both PCS and static light scattering experiments. An aperture setting of 200 μm was used for all photon correlation spectroscopy experiments. The sample time was determined by using the
autosample time selection (press ALT START). For the static light scattering experiments the sample time was fixed at 1 μsec and the aperture was adjusted as shown in table 2.1.

TABLE 2.1: STATIC LIGHT SCATTERING

<table>
<thead>
<tr>
<th>W</th>
<th>APERTURE (μm)</th>
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<tr>
<td>20.0</td>
<td>400</td>
</tr>
<tr>
<td>24.7</td>
<td>400</td>
</tr>
<tr>
<td>27.5</td>
<td>400</td>
</tr>
<tr>
<td>29.0</td>
<td>200</td>
</tr>
<tr>
<td>29.5</td>
<td>200</td>
</tr>
</tbody>
</table>

NOTE: The duration was adjusted for each sample so that 10^5 counts accumulated over the total duration period. On the average, the duration was 200 seconds.
2.2 STATIC LIGHT SCATTERING:

Static light scattering has been used extensively in the study of micellar and microemulsion systems.\textsuperscript{2,4} Static light scattering provides a non-destructive way to extract information about interparticle interactions. In the present study, static light scattering experiments were performed on AOT/Water/n-Decane microemulsions in an effort to learn about the attractive interactions exhibited by the reversed swollen micelles.

Essentials of Static Light Scattering:

A laser is focused such that it illuminates the sample under study. Each particle in the sample scatters light. The photomultiplier tube (PMT), is positioned at a particular angle ($90^\circ$ for the present study) in order to detect the number of photons emitted at the detector angle. This photon count is updated for a prescribed time period.

Ultimately, it is the total photon count or actual number of photons being scattered from the particles for a given time period at a particular angle that we want to
measure. The scattering angle and temperature were kept constant for this study.

However, the measured photon count rate is dependent upon the geometry of the system, (how far the detector is from the sample, for example). In order to compare results from different systems it is desirable to obtain a value from the measured photon count rate of the sample that only depends on the scatterer itself, and not on the source or the detector optics. By calculating the so called Rayleigh factor, geometry considerations are eliminated. The Rayleigh factor is defined as follows:10

\[
R(\theta) = \frac{I(\theta) r^2}{I_{inc} V_{obs}}
\]  

(2.1)

- \( I(\theta) \) = scattered radiance
- \( r \) = distance from the detector
- \( V_{obs} \) = illuminated volume
- \( I_{inc} \) = incident irradiance

The Rayleigh factor has units of cm\(^{-1}\)steradian\(^{-1}\). This represents "the fraction of light scattered per unit length per unit solid angle."10 Typically this Rayleigh factor is called a Rayleigh ratio, but since it does have units, it is not strictly correct to call it a ratio. However, the term Rayleigh ratio is so commonly used that
this paper will continue using it to avoid unnecessary confusion.

The Rayleigh ratio is not directly measured, the photon count/sec, (or count rate), is measured, therefore corrections must be made to the measured count rate. Also the photometer is not an absolute photometer so it must be adjusted for inherent dark counts. See reference #10 for details. The light scattering equipment had vertically polarized light. The index matching fluid-to-vat refractive indices ratio was sufficiently close to 1 and the ratio of the refractive indices of the solvent and calibration liquid (toluene) was also close to 1. The system was non-aqueous, and the solution to cell interface produced no significant reflection. With all the above conditions the Rayleigh ratio is calculated using the following formula:

\[ R(\Theta) = R_{cal}(90^\circ) \sin \Theta \frac{I_{sample}(\Theta) - I_{DopedDecane}(\Theta)}{I_{cal}(\Theta) - I_{DCR}} \]  

(2.2)

where:  
\[ R(\Theta) \] = Rayleigh ratio of sample at \( \Theta \).  
\[ R_{cal}(90^\circ) \] = absolute Rayleigh ratio of calibration liquid at 90°.  
Toluene = 14.0 * 10^{-6} cm^{-1}  
\[ I_{sample}(\Theta) \] = count rate of the sample at the detector angle \( \Theta \).  
\[ I_{DCR} \] = Dark count rate.
2.3 PHOTON CORRELATION SPECTROSCOPY:

Photon correlation spectroscopy (PCS), or dynamic light scattering (DLS), has become a useful tool in determining the diffusion coefficient and the particle size distribution of materials having particles with dimension of a few nanometers to several micrometers. Some advantages of using PCS over other methods that determine the diffusion coefficient are that the measurement does not require calibration and it is easy to operate the equipment and perform the experiment. In fact, as long as the suspension is sufficiently dilute (negligible interparticle interactions or multiple scattering), determination of the diffusion coefficient is independent of particle composition and concentration. In this particular study, the samples were not of such low concentrations that the particles did not interact, so this interaction contributes to the particle motion. There are also hydrodynamic considerations; the movement of the molecules in the fluid creates a perturbation in the fluid which, in turn, affects the subsequent motion of the particles.
Essentials of PCS:

A laser is focused such that it illuminates a relatively dilute suspension. Each particle in the solution scatters light. These light waves interfere with each other and produce a net scattering intensity, \( I(t) \), which is detected by the photomultiplier tube (PMT). Each particle's position in the suspension fluctuates randomly due to Brownian motion (diffusion), interparticle interactions and hydrodynamic contributions. This random fluctuation in position produces a random fluctuation in the phases of each scattered wave as they arrive at the PMT. This means that as the particles diffuse in the suspension, the intensity, \( I(t) \), fluctuates in a way that is related to the particle motion.

An efficient way to analyze this fluctuating intensity signal is to use correlation. Most people are familiar with the idea of correlation. "If two variables or two signals are highly correlated, then a change in one can be used to predict, with confidence, the change in the other. Mathematically, correlation is defined as the average of the product of the two
quantities." If you multiply the intensity function by a delayed version of itself and average the quantity, it is called an autocorrelation function, $C(t)$.

$$C(t) = \left< I(r) \ast I(r+t) \right>$$  \hspace{1cm} (2.3)

Here $I(\tau)$ is the count rate at time $\tau$, and $I(\tau + t)$ is the intensity at some later time, $\tau$ plus delay time $t$. For small time intervals the correlation between $I(\tau)$ and $I(\tau + t)$ is high but as the delay time $(t)$ increases, the correlation decreases. In fact, the correlation function decays exponentially for a suspension of rigid, globular particles and is given by:10

$$C(t) = e^{-2D_t q^2 t}$$  \hspace{1cm} (2.4)

where $q$ is the scattering wave vector defined as follows:

$$q = 4\pi n \frac{1}{\lambda_0} \sin\left(\frac{\Theta}{2}\right)$$  \hspace{1cm} (2.5)

* For a more rigorous explanation of the autocorrelation function, see references #12 and 13.
In Eq. 2.5, \( n \) is the index of refraction of the solvent, \( \lambda \) is the wavelength of light in vacuum and \( \theta \) is the scattering angle. Therefore, by analyzing the intensity autocorrelation function, the collective diffusion coefficient can be determined.

The autocorrelation function described in Eq. 2.4 is based on the system having monodisperse particles. However, most systems are significantly polydisperse and this means that each particle size contributes its own exponential term. Therefore the autocorrelation function for a polydisperse system contains an integral of the exponential in Eq. 2.4. This, of course, increases the complexity of solving the autocorrelation for the diffusion coefficient.\(^{10,12,13}\) For a system of polydisperse particles, the autocorrelation function now looks like:\(^{10}\)

\[
C(t) = \int_{0}^{\infty} G(\Gamma) \, e^{-\Gamma t} \, d\Gamma . \tag{2.5.5}
\]

Here \( G \) is a distribution function, and \( \Gamma = \mathcal{D}q^2 \). This Laplace transform equation has a nontrivial solution. Experimental data is hindered by the effect of dust, real measurement noise and real baseline drifts. All of these plus the fact that we're integrating over
the exponential makes this a difficult problem to solve. The system used for this study uses the method of cumulants to analyze the integral and extract the desired distribution information.

The method of cumulants makes no assumption about the form of the distribution function. A Taylor series is used to expand the exponential about the mean value. The series is integrated yielding a general result. "This result shows that the logarithm of the autocorrelation function can be expressed as a polynomial in the sample time, t. The coefficients of the powers of t are called the cumulants of the distribution. In practice, only the first couple of cumulants are obtained reliably, and these are identical to the moments of the distribution. (In general, the first moment of any distribution is the average and the second is the variance.)" 10

From the first and second moments of the distribution, the diffusion coefficient is calculated. It may be calculated using either a calculated or measured baseline subtraction. The calculated baseline is the infinite time value of the correlation function, whereas the measured baseline is the average of the 6 delay
channels. If the difference between the two baselines is less than 0.02%, the measured baseline may be used, otherwise use the calculated baseline. In this study the calculated baseline was used for all PCS data.
3.1 Interpretation of static light scattering measurements

The properties of a dilute colloidal system are similar to those of an ideal gas. Hence, an analogy can be made between the two systems. The Ideal Gas Law states:

$$\frac{P}{k_B T} = \rho$$  \hspace{1cm} (3.1)

where:  
$P$ = pressure  
k$_B$ = Boltzmann constant  
$T$ = absolute temperature  
$\rho$ = # density of gas molecules.

For non-ideal gases, however, there are particle interactions which add terms to Eq. 3.1 as shown below:

$$\frac{P}{k_B T} = \rho + \left[ B_2(T) \rho^2 + B_3(T) \rho^3 + \ldots \right]. \hspace{1cm} (3.2)$$

If however, a very dilute system of gases is considered, Eq. 3.2 can be truncated after the first interaction term:

$$\frac{P}{k_B T} = \rho \left[ 1 + B_2(T) \rho \right]. \hspace{1cm} (3.3)$$
To make the analogy between a very dilute gaseous system and a dilute colloidal system, specifically a micellar colloidal system, the pressure \( \Pi \) is analogous to the osmotic pressure, \( \Pi \), and \( \rho \) (the number of gas molecules per unit volume of container) is analogous to the number of micelles per volume of solution. This equals the volume fraction of the dispersed phase \( \Phi \) per volume of one micelle \( V_m \), i.e.,

\[
\frac{\Pi}{k_B T} = \frac{\phi}{V_m} \left[ 1 + \frac{1}{2} B \phi \right], \tag{3.4}
\]

where \( B \) is called the second virial coefficient.

If the micelles are assumed to be a constant size then it is known that the intensity of vertically polarized light scattered by particles in a continuous phase is\(^4\)

\[
I(\Theta) = KV_m \phi S(q) P(q). \tag{3.5}
\]

- \( I(\Theta) \) = intensity at the scattering angle
- \( V_m \) = volume of micelle
- \( \phi \) = micellar volume fraction
- \( S(q) \) = structure factor
- \( P(q) \) = intraparticle form factor
K is defined as

\[ K = 2\pi^2 n^2 \left( \frac{dn}{d\phi} \right)^2 (\lambda_0^{-4}) \quad \text{(3.6)} \]

The particles used in the present study have radius under 10 nm, so the intraparticle form factor, \( P(q) \), is essentially equal to 1.4. Also, in the limit as \( q \) approaches zero, the structure factor \( S(q) \) is related to the osmotic pressure by the compressibility relation \(^4\)

\[ S(0) = \frac{k_B T}{V_m} \left( \frac{\partial \Pi}{\partial \phi} \right)^{-1} \quad \text{(3.7)} \]

Where: \( \left[ \frac{\partial \Pi}{\partial \phi} \right]^{-1} = \text{compressibility of system (isothermal osmotic compressibility)} \).

In order to evaluate Eq. 3.7, the osmotic pressure must be known. To understand osmotic pressure it is useful to see Figure 3.1 which exhibits a container that is divided by a semipermeable membrane, (permeable only to solvent). On one side of the membrane there is pure solvent, and on the other side is a microemulsion. Closing the microemulsion side is a piston which can apply pressure to the system. The osmotic pressure \( \Pi \)
is the applied pressure required to stop the solvent from going through the membrane.

![Diagram](image)

FIGURE 3.1: The osmotic pressure \( \Pi \) is the pressure required to stop solvent from going through the membrane.

Now returning to Eq. 3.4, which relates the osmotic pressure to the second virial coefficient and the volume fraction, it is known that this second virial coefficient is related to the interaction potential as follows:

\[
B = -\frac{4\pi}{V_m} \int_0^\infty \left[ e^{\left[-\frac{U(r)}{k_B T}\right]} - 1 \right] r^2 dr \tag{3.8}
\]

\( U(r) \) is the interaction potential.
One of the main conclusions of the modern fluid theories used to explain microemulsion experimental results is that steric repulsions between close particles is a large determining factor in the spatial structure. Using a perturbation to the hard sphere potential is one technique used to deal with attractive or repulsive interactions. In fact, Calje et al.⁹ proposed that the hard sphere potential \( U_{HS} \) added to the attractive potential \( U_A \), describes the interaction potential between micelles. Carnahan and Starling¹⁴ proposed an equation of state that describes the hard sphere contribution to the osmotic pressure. The total osmotic pressure is defined as²

\[
\Pi = \Pi_{HS} + \Pi_A .
\] (3.9)

The Carnahan-Starling expression states that for a hard sphere gas the equation of state is¹⁴

\[
P_{HS} = \rho k_B T \left[ \frac{[1+\phi+\phi^2-\phi^3]}{(1-\phi)^3} \right] .
\] (3.10)

Now, using the analogy presented above for a non-ideal gas compared to a hard sphere fluid, Eq. 3.10 can be rewritten as
\[
\Pi_{HS} = \frac{k_B T}{V_{HS}} \phi_{HS} \left[ \frac{1 + \phi_{HS} + \phi_{HS}^2 - \phi_{HS}^3}{\left(1 - \phi_{HS}\right)^3} \right]
\]

where \( \phi_{HS} \) = volume fraction of hard spheres
\( V_{HS} \) = volume of a hard sphere.

The attractive osmotic pressure must also be considered. If it is treated as a perturbation, it is

\[
\Pi_A = \frac{k_B T}{V_m} \frac{A}{2} \phi^2
\]

(3.12)

where

\[
A = \frac{4\pi}{k_B T} \frac{1}{V_m} \int_{2R_{HS}}^{\infty} U_A(r) r^2 \, dr
\]

(3.13)

\( U_A(r) \) is the attractive portion of the interaction potential. The hard sphere volume fraction, \( \phi_{HS} \), is related to the total volume fraction, \( \phi \), by

\[
a = \frac{\phi_{HS}}{\phi}
\]

(3.14)

Using the total osmotic pressure, the second virial coefficient is calculated to be \( B = 8a + A \), where \( A \) is as defined in Eq. 3.13 and is the attractive perturbation to the second virial coefficient. In this model the photon count rate is

\[
I(\Theta) = \frac{K V_m \phi (1 - a \phi)^4}{\left\{ 1 + 4a \phi + 4a^2\phi^2 - 4a^3\phi^3 + A\phi(1 + a \phi)^4 \right\}}
\]

(3.15)
Pictorially the hard sphere interaction is as shown in Figure 3.2.

\[ \frac{U(r)}{k_B T} \]

\( \sigma \)
\( r \)

FIGURE 3.2: HARD SPHERE POTENTIAL, there is infinite repulsion when the spheres are in contact (the distance between the center of the spheres is \( \sigma \) ) and zero interaction potential when \( \sigma < r < \infty \).

In the hard sphere model the interaction potential is infinitely repulsive when the spheres are touching and as soon as their contact breaks (moving apart), there is zero interaction potential. However, there are micelles in the microemulsion, not hard spheres, and experimentally the interaction has been shown to be of the form represented in Figure 3.3.\(^4\)
FIGURE 3.3: Micellar interaction potential

One may consider modelling this micellar system with a square well attractive interaction potential as shown in the following figure.

FIGURE 3.4: Square well potential

The square well potential requires a range parameter to describe the width of the well in addition to knowing the diameter of the particles, the depth of the well, and a constant. This presents a rather complex problem involving four fitting parameters. The adhesive sphere model eliminates the range parameter.
The adhesive sphere model has been shown to effectively describe the microemulsion interaction potential throughout a large range of volume fractions in SAXS experiments.\textsuperscript{19,20,21} This model is shown in Figure 3.5.

\begin{equation}
\frac{U(r)}{k_B T}
\end{equation}

FIGURE 3.5: Adhesive sphere model for the interaction potential. The attractive well is infinitely narrow (let $d$ approach $\sigma$).

The range parameter is eliminated by letting the width of the attractive potential, $(d - \sigma)$, approach zero. This makes the attractive range infinitely narrow. Baxter\textsuperscript{15} has defined the interaction potential for the adhesive sphere model:
This model has been successfully used in previous experiments. Robertus, et. al. have used the adhesive sphere model and considered the effects of polydispersity. The potential shown above has a singularity when \( d = \sigma \), however the second virial coefficient, (Eq. 3.8), remains finite due to the exponential term. The parameter \( \tau \), is called the stickiness parameter. It is positive, dimensionless and is equal to \( \frac{2}{A} \). Since \( A \) is a measure of the stickiness of the particles, the inverse of \( \tau \) is also a measure of the stickiness between particles.

By fitting an experimental photon count rate vs. \( \phi \) curve with Eq. 15, the attractive perturbation to the second virial coefficient \( (A) \), and \( (a) \), the ratio of the hard sphere volume fraction to the total volume fraction, can be determined. Remember that the measured photon count rate is not independent of the geometry of the experimental setup, therefore the measured photon count rate is converted to a Rayleigh ratio and then
plotted against the volume fraction. See Figure 3.6 for an example of a typical Rayleigh ratio vs. $\phi$ curve.

FIGURE 3.6: Rayleigh ratio vs. volume fraction for an H$_2$O/AOT/Decane microemulsion with $W = 24.7$ and $\phi$ ranging from 0.03 to 0.25.
3.2 Interpretation of PCS measurements

At relatively low concentrations the collective diffusion coefficient is described as follows:16,17

\[ D_c = D_0 [1 + k \phi] \] \hspace{1cm} (3.17)

where \( D_c \) is the collective diffusion coefficient, \( D_0 \) is the Brownian or single particle diffusion coefficient and \( \phi \) is the volume fraction of particles in the suspension. \( k \) is a numerical coefficient that depends on particle interactions. Using the adhesive sphere model, \( k \) is dependent on the stickiness parameter (\( \zeta^{-1} \) describes the adhesion between interacting surfactant tails) as shown below:1

\[ k = 1.454 - \left( \frac{1.125}{\zeta} \right) \] \hspace{1cm} (3.18)

The single particle diffusion coefficient \( D_0 \) is described by the Stokes-Einstein relation which states that as the particle diameter decreases, the diffusivity increases:

\[ D_0 = \frac{k_B T}{3 \pi \eta r_h} \] \hspace{1cm} (3.19)
Here, \( \eta \) is the shear viscosity of the solvent, and \( r_h \) is the hydrodynamic radius of the particles, which are assumed to be spherical in shape.\textsuperscript{11} When the diffusion coefficient is known, equations 3.17 and 3.19, are used to calculate the effective diameter.

Throughout the relatively low range of volume fractions prepared, the diffusion coefficient was calculated for each sample batch of particular micelle size. The diffusion coefficient is calculated using the method of cumulants from the intensity autocorrelation data. Typical autocorrelation functions are shown on the following pages (Figure 3.8) These are plotted on a semi-log graph to show that multiple exponentials exist.
FIGURE 3.7: The natural logarithm of the intensity autocorrelation function. This data is used to calculate the collective diffusion coefficient, $D_c$, for each sample.
At a given $W$, the diffusion coefficient was plotted against the volume fraction. A best straight line fit was drawn using only the low volume fraction data (this is because higher order terms were dropped in the theoretical development). The resulting curve was extrapolated to zero concentration to find $D_0$. A typical example is shown in the following figure.

![Graph](image)

FIGURE 3.8: Batch 10, $W = 27.5$, Using photon correlation spectroscopy the diffusion coefficient was obtained for each volume fraction. Only one trial was performed.

From Eq. 3.17, the slope of the curve is equal to $kD_0$. Knowing the slope and $D_0$, the value for $k$ can be determined. Knowing $k$ and Eq. 3.18, the stickiness parameter, $\tau$, can be determined. From the stickiness parameter, $A$ (the attractive perturbation to the second
virial coefficient) can be calculated. The value for $A$ determined using PCS can be compared to the value obtained from static light scattering experiments.
Chapter 4. THE EXPERIMENT

4.1 Sample preparation and compositions

A swollen reversed micelle system was chosen for this study. The three component microemulsion consisted of H$_2$O, AOT which is Bis(2-ethylhexyl)sulfosuccinate sodium salt, and n-decane (a ten carbon chain oil). The surfactant (AOT) has a branched tail configuration. Figure 4.1 shows two AOT molecules with their tails overlapping. Sample compositions were specified by choosing the water to AOT molar ratio, (W), as well as the AOT-plus-water volume fraction of the solution ($\phi$).

FIGURE 4.1: The AOT structure. (reproduced ref. #3)
The chemical formula for AOT is \( \text{C}_{20}\text{H}_{37}\text{NaO}_{7}\text{S} \). The water to AOT molar ratio was determined as follows:

\[
W = \frac{[\text{water}]}{[\text{AOT}]} = \frac{V_{\text{water}} \rho_{\text{water}}}{\frac{M_{\text{water}}}{m_{\text{AOT}}} \frac{m_{\text{AOT}}}{M_{M_{\text{AOT}}}}}.
\]  

\( V_{\text{water}} \) = volume of water  
\( \rho_{\text{water}} \) = density of water = 1 g/cc  
\( M_{\text{water}} \) = molecular mass of water = 18 g/mole  
\( m_{\text{AOT}} \) = mass of AOT  
\( M_{M_{\text{AOT}}} \) = molecular mass of AOT = 444.5 g/mole.

The size of the reversed swollen micelles linearly increases with \( W \). The surface area is determined by the amount of AOT present and the size of the reversed swollen micelle is directly related to the surface area. In addition, as \( W \) changes the density of micellar droplets changes. The other factor determining the composition of the microemulsion is \( \phi \), the volume fraction of micelles (water + AOT):

\[
\phi = \frac{V_{\text{water}} + m_{\text{AOT}} \left( \frac{1}{\rho_{\text{AOT}}} \right)}{V_{\text{water}} + m_{\text{AOT}} \left( \frac{1}{\rho_{\text{AOT}}} \right) + V_{\text{Decane}}}.
\]

Where: Density of dry AOT = 1.13 g/cc
An oversimplified illustration of the particular microemulsion used is shown in the following figure.

FIGURE 4.2: AOT/water/decane microemulsion: Contains swollen reversed micelles

Sample preparation is decidedly the most difficult portion of the experiment. Accuracy is critical, however even with accurately made samples, the results can be obscured by impurities. It is critical that impurities be minimized, as they scatter light and make it difficult, if not impossible, to distinguish scattering from the particles in solution.

It was found that significantly different results were obtained when using unpurified AOT as opposed to
purified AOT. The unpurified results were erratic and drifted over time. Thus for all reported results, samples were made with purified AOT. See APPENDIX D for the AOT purification procedure.

We used 18 M-$\Omega$ deionized water supplied by the R.I.T. A-level science stockroom. The AOT was supplied by Fluka with $>99\%$ purity. The decane was supplied by Aldrich with $>99\%$ purity. In addition, the samples were each filtered using Gelman Sciences ACRODISC LC PVDF 0.2 $\mu$m pore size syringe filters. They were filtered twice through the same filter.

All samples were made by diluting a stock solution to the desired volume fractions. The diluted samples were put in glass containers. Each sample was poured into a sample cell cleaned according to cleaning procedure #1 (see APPENDIX C). The cap was placed on the sample cell, the cell was lightly shaken and the microemulsion poured into a disposable 10 ml syringe fitted with a 0.2 $\mu$m filter. The solution was filtered into the sample cell, shaken and poured back into the syringe to be filtered for the second time. The sample was visually inspected for impurities, and if present the solution was filtered again. The sample was labeled appropriately and allowed
to equilibrate thermally to 23.1°C and stabilize. This takes about 24 hours.

The sample batches were prepared according to \( W \), which is related to particle size. For a particular batch the \( W \) value was kept constant and the volume fraction ranged anywhere from \( \phi = 0.03 \) to 0.45. Table 4.1 shows the composition of the original stock solution for each sample batch. Doped decane was added to calculated amounts of the stock solution to achieve the desired volume fraction. The decane was doped to 0.02 weight percent in order to stay above the critical micelle concentration (the concentration of surfactant necessary for micelle formation).
### TABLE 4.1: SAMPLE COMPOSITIONS

<table>
<thead>
<tr>
<th>BATCH #</th>
<th>H₂O cc</th>
<th>AOT g</th>
<th>DECANE cc</th>
<th>W</th>
<th>Φ of STOCK</th>
</tr>
</thead>
<tbody>
<tr>
<td>B5</td>
<td>10.000</td>
<td>9.9950</td>
<td>56.500</td>
<td>24.7</td>
<td>0.25</td>
</tr>
<tr>
<td>B6</td>
<td>14.600</td>
<td>12.0003</td>
<td>46.800</td>
<td>30.0</td>
<td>0.35</td>
</tr>
<tr>
<td>B7</td>
<td>8.910</td>
<td>11.0046</td>
<td>34.620</td>
<td>20.0</td>
<td>0.35</td>
</tr>
<tr>
<td>B8</td>
<td>7.300</td>
<td>10.0120</td>
<td>30.000</td>
<td>18.0</td>
<td>0.35</td>
</tr>
<tr>
<td>B8.1</td>
<td>6.850</td>
<td>9.4024</td>
<td>18.540</td>
<td>18.0</td>
<td>0.45</td>
</tr>
<tr>
<td>B9</td>
<td>9.110</td>
<td>15.0002</td>
<td>41.570</td>
<td>15.0</td>
<td>0.35</td>
</tr>
<tr>
<td>B10</td>
<td>16.870</td>
<td>15.1446</td>
<td>56.220</td>
<td>27.5</td>
<td>0.35</td>
</tr>
<tr>
<td>B11</td>
<td>17.617</td>
<td>15.0012</td>
<td>57.370</td>
<td>29.0</td>
<td>0.35</td>
</tr>
<tr>
<td>B12</td>
<td>10.997</td>
<td>9.2054</td>
<td>46.867</td>
<td>29.5</td>
<td>0.29</td>
</tr>
</tbody>
</table>
4.2 Experimental results

From static light scattering, experimental results for the Rayleigh ratio vs. volume fraction were obtained. See Figure 4.3 for the static light scattering experimental results. Notice that A is an increasing function of W. The error bars shown in graphs A and B represent the reproducibility between two trials, which is approximately 15%. The circles in these two graphs represent the average of the trials and the error bars show the maximum and minimum values. Graphs C-E were constructed on the basis of a single trial.

This data was put into a fitting program (See APPENDIX E) which fits the data to Eq. 3.16 using a chi square minimization routine to get the best fit. From the best fit curve, values for A, (the attractive perturbation to the second virial coefficient), and a, (the ratio of the hard sphere volume fraction to the total volume fraction), were determined.
FIGURE 4.3:
Graphs A–E show the dependence of the Rayleigh ratio on the volume fraction. They are displayed in order of increasing $W$. Experimental data are represented with circles. Graphs A and B have error bars which show the reproducibility between two trials. Graphs C–E were constructed on the basis of a single trial. The theoretical fit to the data, using Eq. 3.15, is shown with the solid line.
From PCS experiments, data for the relationship between the diffusion coefficient and volume fraction of AOT/WATER/n-DECANE microemulsions were obtained. This data is graphically presented in Figure 4.4. The fit was done manually to low volume fractions. From the slope and intercept, $k$ and $D_0$ are determined respectively. Knowing $k$, the stickiness parameter is calculated (see Equations 3.17, 3.18 and 3.19). From the stickiness parameter, $A$ is determined.
FIGURE 4.4: From PCS, the relationship between the diffusion coefficient and $\phi$ was determined. Experimental data is shown with circles and the theoretical fit is expressed with a solid line.
4.3: Interpretation of results

Huang et al.\textsuperscript{3} suggest that as two micelles approach one another the surfactant tails are able to penetrate to a certain extent, this is the cause of the adhesiveness or attractive portion of the interaction potential. See Figure 4.5.

\textbf{FIGURE 4.5}: The assumption is that there is a maximum penetration depth \((h)\) due to the branching structure of the AOT tails. It is also assumed that \(A\), the attractive perturbation to the second virial coefficient, is proportional to the overlap volume \(V(R,h)\). The total radius is equal to \(R\) and the surfactant tails have length \(L\).
It can be determined that the attractive perturbation to the second virial coefficient equals

\[
A = C \left[ \frac{3L}{1 - a^3} - \frac{h}{2} \right],
\tag{4.3}
\]

where C is a constant. See Appendix F for a derivation of this equation.

The values for A and a obtained from the theoretical fit to the static light scattering data (Rayleigh ratio vs. Φ) were plotted to see if they obeyed the relationship described in Eq. 4.3. To do this a data point was picked at low a, the a-value and it's corresponding A-value were put into Eq. 4.3 where the (-h/2) term was omitted as it has a negligible affect on the outcome of the A value. Also, the (3L) and the proportionality were incorporated into the constant C which makes the fitting equation of the form

\[
A = \frac{C}{1 - a^3}. \tag{4.4}
\]

With the data point (a,A) put in the equation, it was solved for C. For this low "a" data point it was found that C = 0.65. A high "a" value
was also picked, and solving for C, a value of 1.1 was calculated.

Using these two C values, curves were generated according to Eq. 4.4. These curves are displayed along with the data in Figure 4.6.

FIGURE 4.6: The attractive perturbation to the second virial coefficient as a function of the ratio of the hard sphere volume fraction to the total volume fraction. Experimental data are displayed with circles and the generated "theoretical" curves are the solid lines.
The actual $C$ value is believed to lie within the range of $0.65 < C < 1.1$. It was realized later that a better way to find the constant $C$ would be to plot $A$ vs. $(1 - a^{1/3})^{-1}$. Using Eq. 4.4, a straight line fit to the points yields a slope that equals $C$. This is shown in Figure 4.6.1.

FIGURE 4.6.1: A best straight line was drawn to yield $C = 0.78$. This falls well within the range of $C$ values ($0.65 < C < 1.1$) found previously.
Due to time limitations, the actual critical points for $a$ and $\phi$ were not found from Figure 4.6.1. However, the constant $C$ is definitely within the range of $C$-values obtained earlier.

The range of $W$ values from which data was obtainable was limited. With $W < 18$, the intensity was so low it was difficult to get a photon count and the curve did not have a bending over trend observed with the other light scattering data. See Figure 4.6.5.

FIGURE 4.6.5: Static light scattering data unable to be fit using Eq. 3.15.
On the other hand, when running a sample batch with $W = 30$, the static light scattering data was highly erratic and it was not possible to fit the data using Eq. 3.15. This data is shown in the following figure.

![Figure 4.7: Static light scattering data unable to be fit using Eq. 3.15.](image)

It is believed that there is a phase change occurring somewhere between $W = 29.5$ and $W = 30$ that is causing the erratic trends observed in the $W = 30$ data. Thus, $W$'s were chosen to fall in the range of 20 to 29.5. As displayed in Figure 4.3, the static light scattering data for $W = 29.5$ follows the trend of the theory. This leads one to believe that there may be a critical point somewhere between $W = 29.5$ and $W = 30$. 
The critical points are defined by the conditions:

\[
\left[ \frac{\partial \Pi}{\partial \phi} \right] = 0 \tag{4.5}
\]

and

\[
\left[ \frac{\partial^2 \Pi}{\partial \phi^2} \right] = 0 \tag{4.6}
\]

Using Eq. 3.9, 3.11, and 3.12 it can be shown that first derivative of the osmotic pressure with respect to the volume fraction is

\[
\frac{\partial \Pi}{\partial \phi} = \frac{1 + 4a\phi + 4a^2\phi^2 - 4a^3\phi^3 + a^4\phi^4 + A\phi(1-a\phi)^4}{(1-a\phi)^4} \tag{4.7}
\]

The second derivative of the osmotic pressure with respect to the volume fraction is

\[
\frac{\partial^2 \Pi}{\partial \phi^2} = \frac{4a + 8a^2\phi - 12a^3\phi^2 + 4a^4\phi^3 + A(1-a\phi)^4 - 4A\phi a(1-a\phi)^3}{(1-a\phi)^4} + \frac{1 + 4a\phi + 4a^2\phi^2 - 4a^3\phi^3 + a^4\phi^4 + A\phi(1-a\phi)^4}{(1-a\phi)^5} \tag{4.8}
\]
Using the constraint in Eq. 4.4, the first and second derivatives were set equal to zero. The constant C was set equal to 0.65 and 1.1. A range of a-values were also chosen. The vertical coordinate in these graphs (x) represents \( a \phi \). These curves are shown in Figure 4.8. The curves indicated that the critical a-value lies within the range \( 0.82 < a < 0.90 \).

From the critical X and a-values, \( \Phi_c \) and \( \Lambda_c \) were calculated. The critical values are:

\[
0.144 < \Phi_c < 0.155 \quad \text{and} \quad 17.39 < \Lambda_c < 19.03.
\]

Huang\(^2\), through an analysis that excluded the factor of "a", found \( \Lambda_c = 21.2 \) and \( \Phi_c = 0.13 \). We believe the values above to be better representations of the actual values because the theory used accounts for the ratio of the hard sphere volume to the total volume of a micelle.
Figure 4.8

$X = a \phi$

Squares and pluses denote setting the first derivative of $\tau$ with respect to $\phi$ equal to zero. Diamonds represent setting the second derivative of $\tau$ with respect to $\phi$ equal to zero. The critical point is where the first derivative curve crosses the second derivative curve. This is only an approximation due to the constant $C_0$ which was obtained from fitting the experimental $A$ vs. $a$ data where a range of $C$ values seemed to fit. The range was from $0.65 < C < 1.1$. 

$C = 0.65$

$C = 1.1$
The critical values for A are plotted on the following A vs. W graphs for both static light scattering and PCS. The critical values seem to follow in the trend of the static light scattering data. The PCS data however, do not have any noticeable relationship to the calculated critical points.
**FIGURE 4.9:** Static light scattering and photon correlation spectroscopy calculated values for the attractive perturbation to the second virial coefficient as a function of water-to-AOT molar ratio.
The values for $A$ that were obtained from static light scattering ranged from $A = 4.795$ to $10.134$ and seemed to correspond with the critical point analysis. The values from PCS data ranged from $A = 7.01$ to $7.44$ and did not exhibit any particular trend. Although the $A$ values from the independent studies did not have exact correspondence, they were certainly in the same range. The photon correlation spectroscopy experiments were all performed on a single trial basis. More trials would be beneficial in the sense that any erratic values would have a diminished effect. In this experiment, PCS data for $W < 24.7$ were not attainable.
Chapter 5. CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

From static and dynamic (PCS) light scattering results, it has been determined that the attractive perturbation to a hard sphere model is capable of describing the AOT/WATER/n-DECANE microemulsion. The agreement of the static light scattering data with the theory is quite good within the range of volume fractions and W values that were experimentally accessible. The independently determined values for A using PCS, although not as outstanding as the static light scattering, confirmed that the values obtained are in reasonable agreement.

I must question results that Huang reports in reference #2. He claimed to fit static light scattering data with a function that was dependent on only three parameters ($A$, $\phi$, constant). I tried to fit my experimental data with his function and was unsuccessful. However, the four parameter fit which includes the parameter, $a$, closely fit the data.

One of the limitations of the data analysis presented in previous sections of this paper is that the theories apply only to monodisperse systems. This does
not seem to affect the conclusions. Experimental errors, which were within 15%, are comparable to the effects of the polydispersity on the photon count at the volume fractions examined.

Another possibility is that there are many assumptions, including some about the hydrodynamic aspects of the particle diffusion, in the formulation of Eq. 3.18 that predicts the value for $k$, the numerical coefficient affecting the collective diffusion coefficient. The hydrodynamic aspects in particular are difficult to calculate theoretically. Or, it may be as simple as the way the best line was fit to the PCS data. The fit was done manually to low volume fractions. There is a lot of room for error in deciding what constitutes low volume fractions. Additionally, the fact that only one trial was performed made it difficult to draw a best fit line because error bars were not present.

The results presented above are consistent with SANS results\(^3\) which suggest that the overlapping of the surfactant tails is the source of the short range interaction potential observed. The strength of this interaction is believed to be related to the overlap volume of the surfactant tails, but the results also
suggest that there may be other contributors to the strength of the interaction.

An exceptional area for future research would be to study the microemulsion in the critical region for "a". The actual critical values may be determined for a, A and \( \phi \). These results can be compared to those obtained using SANS. It would also be desirable to do an intense study on the microemulsion using PCS. By making successive trials it is believed that the attractive perturbation to the second virial coefficient can be more closely related to that obtained with static light scattering using an attractive perturbation to a hard sphere model.
APPENDIX A

START UP PROCEDURE

1. Turn laser on with key switch. Allow 1.5 to 2 hours warm up time for stabilization (Be certain beam stop is in place!)

2. To supply high voltage to PMT
   a. Turn all knobs to zero before turning power on
   b. Turn power on and wait a few seconds
   c. Meter switch should be on KV scale
   d. Slowly turn top knob (0-2500 V) to 2000 volts (Wait at each setting for display to adjust)
   e. Fine tune using bottom knob to reach 2050 volts (display reads "-2.05")
      Note: it should read negative voltage

3. Turn BI-2030AT digital correlator on

4. Turn monitor on

5. Turn computer on

6. Turn temperature controller on using the main switch in back, the power on and the cooling on switches. Adjust to the appropriate temperature.

7. Using the BI software
   a. In DOSSHELL, choose "BROOKHAVEN PARTICLE SIZING"
   b. Press PAGE on the function keypad to get menu
   c. Press 1, to set parameters
   d. Set the duration by pressing DURATION on the
function keypad

e. Set the sample time using function keypad or press alt start to use auto sample time

f. When through, press Ctrl C which goes to the "C" prompt, type DOSSHELL to get back to the shell
INDEX OF REFRACTION:

DECALIN = 1.475 (LIQUID IN VAT)
DECANE = 1.4110 (SCATTERING SOLUTION) (FROM BOTTLE LABEL)
SAMPLE CELL = 1.52 (BORO SILICATE GLASS)
BENZENE = 1.5011 (CALIBRATION LIQUID) (FROM CRC, P. C-105)
POLYSTYRENE = 1.332
TOLUENE = 1.4961 (CALIBRATION LIQUID) (FROM CRC, P. D-518)

VIScosITY:

DECANE = 0.92 CENTIPOISE AT 20° C
BENZENE = 0.652 CENTIPOISE AT 20° C (CRC, P. F-38)
POLYSTYRENE = 0.9330 CENTIPOISE
TOLUENE = 0.540 CENTIPOISE (CRC, P. F-41)
NOTE: FOR BOTH STATIC LIGHT SCATTERING AND PCS MEASUREMENTS:

1. KEEP COUNT RATE < 100 KHz OF 100,000 CPS (ADJUST APERTURE IF NECESSARY)

2. COUNT LONG ENOUGH TO ACCUMULATE 1,000,000 COUNTS (ADJUST DURATION IF NECESSARY)
APPENDIX C

CLEANING PROCEDURE #1 (CP#1)

For use with all glassware and utensils.

NOTE: DUE TO THE DELICATE NATURE OF THE SAMPLE CELLS, Omit steps # 1-3.

1. Wash with soap (non-abrasive) and water
2. Rinse well, and then rinse again
3. Dry with a paper towel
4. Rinse with water again and dry
5. Rinse with deionized water and let dry (no paper towel!)
6. Rinse with acetone and let dry
7. Rinse with methylene chloride and let dry
8. Rinse with cyclohexane and let dry (make sure it is completely dry before using)
APPENDIX D

AOT PURIFICATION PROCEDURE

1. Dissolve 1 part AOT in 3 parts methanol
2. Filter solution through 0.2 um filters
3. Evaporate methanol by rotating vacuum method at room temperature
4. Redissolve 1 part AOT and 1 part activated charcoal in 3 parts hexane
5. Filter solution through Whatman 1.6um Glass Microfiber GF/A filter paper
6. Rotary evaporate hexane at room temperature

NOTE: YIELD IS APPROXIMATELY 50 %.
APPENDIX E

INSTRUCTIONS TO FIT RAYLEIGH RATIO VS. $\phi$ CURVE

The fitting program is written in FORTRAN and consists of a main routine (MAINFIT), which calls on three subroutines (FITFUNC, CURFIT and READ_1D)

1. ENTER DATA INTO C:\AWORKS WORDS*2 FILE IN THE FORM:

   $\phi$, RAYLEIGH RATIO, DELTA RAYLEIGH RATIO

   ex. .35,1.861E-4,2.000E-6
   .33,1.898E-4,5.050E-6

   **DO NOT PUT ANY WORDS OR LABELS IN THIS FILE**

2. EXPORT FILE TO C:\FORT\SOURCE\FILENAME

3. GET INTO C:\FORT\SOURCE\FILENAME DIRECTORY

4. PRESS CTRL PRTSC (TO SEND EVERYTHING TO THE PRINTER)

5. TYPE MAINFIT

6. ENTER APPROPRIATE PARAMETERS
   (NOTE: Make sure that the file you save to has a .DAT extension so that you can import it to GRAPHER)

7. CONFIGURE GRAPHER SO THAT IT LOOKS IN THE C:\FORT\SOURCE DIRECTORY

8. IMPORT DATA FILES AND ADJUST PARAMETERS IN GRAPHER TO PLOT
APPENDIX F

Derivation of A vs. a relationship

The model assumes that: 1. there is a maximum penetration depth of the surfactant tails and 2. the attractive perturbation to the second virial coefficient, \( (A) \), is proportional to the interaction strength. The overlap volume, \( V(R,h) \), is represented pictorially by the following figure:

Here the maximum penetration depth is represented by \( h \), and the total length of the surfactant tails is \( L \). The
overlap volume, $V(R,h)$, noted in the hashed region, can be expressed as \(^{22}\)

$$V(R,h) = \frac{\pi h^2}{6} \left[ 3R - \frac{h}{2} \right] . \quad (6.1)$$

It has been defined that

$$a = \frac{V_{HS}}{V_T} . \quad (6.2)$$

The hard sphere volume divided by the total volume is also equivalent to

$$a = \left( \frac{R_{HS}}{R} \right)^3 . \quad (6.3)$$

The hard sphere radius is the total radius minus the length of the surfactant tails:

$$R_{HS} = R - L . \quad (6.4)$$

Substituting Eq. 6.4 into 6.3 and 6.2, a is described as:

$$a = \left( \frac{R - L}{R} \right)^3 . \quad (6.5)$$

Now, solve for $R$. 
Substituting back into Eq. 6.1, we find that

\[ A \propto V(R, h) = C \frac{\pi h^2}{6} \left[ \frac{3L}{\left( 1 - \frac{1}{a^3} \right)} - \frac{h}{2} \right]. \]
REFERENCES


