LIGHT SCATTERING STUDY OF POLYMER-COLLOID SYSTEMS:
SURFACTANTS BEHAVIOR AND INTERACTION WITH POLYMERS AND
SMALL MOLECULES

AN ABSTRACT

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OF THE GRADUATE SCHOOL

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FOR THE DEGREE

OF

DOCTOR OF PHILOSOPHY

BY

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Abstract

This work studies the self-assembly behavior of the surfactant around its critical micelle concentration (CMC) and the interaction between surfactants and hydrophobic dopants. A light scattering based model is proposed to explain the mechanism behind the unknown light scattering peak around the CMC and quantify the important properties of surfactant micelle solutions. The polymeric suppression effect on the aggregate structures of surfactants and hydrophobic dopants is discussed in this context.

The applications of Simultaneous Multiple Sample Light Scattering (SMSLS) to the fundamental properties of surfactants are also discussed in this work. SMSLS has been used for the first time to quickly determine the phase diagrams of binary/ternary systems, the cloud point of the neutral surfactant, and the CMC of the surfactant at different temperatures.

The last part of this thesis is about the development of second generation ACOMP (SGA) and its application in monitoring the response of “smart polymers” to external stimuli during the synthesis. The very first data produced by SGA using different solution conditions are shown in this work. The response of acrylamide/styrene sulfonate copolyelectrolyte to different ionic strengths during the synthesis is followed by the SGA simultaneously for the first time.
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1. Introduction

The surfactant, as a compound containing both hydrophobic groups and hydrophilic groups, can significantly reduce the surface/interfacial tension by accumulating on the phase boundary. The self-assembly of surfactants around the critical micelle concentration (CMC) and the properties of surfactant micelles after CMC are the most important characteristics of surfactants in terms of their practical use.

Polymers composed by many repeating monomer units are the one of the most important materials in the world because of their unique physical/mechanical properties and diverse chemical functionalities.

Surfactants together with polymers have been used widely in a wide range of applications. Certain polymer/surfactant mixtures can produce the stability, rheology, and other properties needed for specific application. The performance of the formulated products not only depends on the behavior of each component, but also relies on their interaction. Exploring the properties of both surfactants and polymers, as well as their interaction, is essential for better formulation work, and is the main goal of this work.

This work starts from the self-assembly behavior of surfactant around its CMC and the interaction between surfactant and hydrophobic dopant. A light scattering based model is proposed to explain the mechanism behind the unknown light scattering peak around the CMC and quantify the important properties of surfactant
micelle solutions. Following, the polymeric suppression effect on the aggregate structures of surfactants and hydrophobic dopants is discussed. The applications of Simultaneous Multiple Sample Light Scattering on exploring the fundamental properties of surfactants are also discussed in this work. The last part of this thesis is about the development of second generation ACOMP (SGA) and its application in monitoring the response of “smart polymers” to external stimuli. This project shows the very first data produced by SGA.

The work presented in this thesis has been published in the following papers and conferences presentations:


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Zhu, Z.; Reed, W. F.  Light scattering maxima near micellar CMC and relationship to target molecule loading capacity and release. 245th *American
Chemical Society national meeting, New Orleans, LA, April 7-11 (2013)

Zhu, Z.; Alb, A. M. Synthesis and characterization of guar gum-g-poly(acrylic acid) copolymers. 245th American Chemical Society national meeting, New Orleans, LA, April 7-11 (2012)

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Zhu, Z.; Flores, J.; McCormick, C. L.; Reed, W. F.; Alb, A. M. Effect of ionic strength on polyzwitterions conformations and interactions for controlled-structure polymeric betaines via RAFT. 241st American Chemical Society national meeting, Anaheim, CA, March 27-31 (2011)
2. Theory

2.1 Introduction

This chapter discusses the fundamental properties of polymers and surfactants in aqueous solution. Understanding these theories is helpful to better explore the self-assembly behavior of surfactants as well as the mechanism behind polymer-surfactant interactions.

Light scattering as an evolving non-invasive, non-destructive technique for characterizing macromolecules and a wide range of particles in solution is the main technique involved in this work. The basic theory of Rayleigh light scattering is also discussed in this part.

2.2 Polymer

2.2.1 Introduction

Polymer is a large molecule composed by repeated smaller chemical units known as monomers. Polymers can be divided into two categories, synthetic polymers such as polyvinyl chloride and natural biopolymers such as proteins and polysaccharides. Both natural biopolymers and synthetic polymers are formed through polymerization of many monomers as shown in Figure 2.1. The n repeating monomers are connected by covalent bond to form large macromolecules, and n is defined as the degree of polymerization. While polymers with identical structure and composition may have
similar chemical properties, their physical properties continuously change with the increase of molecular weight. In general, higher degree of polymerization comes with higher melting temperature and higher mechanical strength of polymers.

![Styrene polymerization](image)

Figure 2.1 Styrene polymerization

The molecular weight of synthetic polymers can be well controlled from a few hundred to tens of millions (g/mole). The number and types of active function groups can also be optimized to form a new product with special functions. For example, the amino-functionalized polyethylene has been used to enhance the adhesion between polyolefins and polyurethanes [1]; it is these diverse and unique properties that make polymers one of the most widely used materials in our daily life.

### 2.2.2 Molecular weight distribution

While polymeric materials are formed by polymerization of many repeating units with the same chemical structures, the physical properties of synthetic polymers are totally different from the monomers. Most monomers are in either gaseous or liquid state. Even for the few in solid state, they do not have enough strength and toughness
to be used widely. However, the synthetic polymers from these monomers can have
the same strength as steel. More importantly, their elasticity and toughness are similar
to rubber. These changes are mainly due to the high molecular weight of synthetic
polymers.

Comparing with the regular low molecular weight compounds, there are two
significant differences for polymers. First, the average molecular weight of polymer is
much higher than the one of regular chemical compound. Also, the molecular weight
of polymer is a polydisperse distribution rather than a single number. The low
molecular weight portion of the polymer improves its ductility, while the high
molecular weight portion enhanced its strength. Therefore, it is important to study and
control the molecular weight of polymers.

Different models for mass distribution of polymers based on the probability
distribution function of the chains length are summarized below.

i) The number-average molecular weight, $M_n$, defined as:

$$M_n = \frac{\sum n_i M_i}{\sum n_i} \quad (1)$$

ii) The weight-average molecular weight, $M_w$, defined as:

$$M_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} \quad (2)$$

iii) $z$-average molecular weight, $M_z$, defined as:
\[ M_Z = \frac{\sum n_i M_i^3}{\sum n_i M_i^2} \]

where \( n_i \) is the number of polymer chains of mass \( M_i = iM \), and \( M \) is the mass of the monomer.

For the number weight average molecular weight, each polymer chain is counted equally regardless the chain length. The shorter chains with smaller mass play important roles in \( M_n \). The number average is the simplest average method, representing the total molecular mass present divided by the total number of molecules. Many thermodynamic measurements like osmotic pressure, boiling point elevation and freezing point depression are based on the number of molecules present, and hence depend on the number-average molecular weight [2]. The weight-average molecular weight takes the mass of each chain into account, so it is a more structure related molecular weight and more sensitive to longer chains in the polymer. \( Z \)-average molecular weight is correlated to polymer processing properties since the flex life and stiffness of polymers are dominated by the longest chain in the polymer [3].

The ratio of \( M_w/M_n \) is defined as polydispersity index (PDI), which represents how polydisperse the polymer sample is. For a perfectly monodisperse polymer, \( M_n = M_w = M_z \), PDI=1, otherwise, PDI>1. Greater PDI corresponds to the broader mass distribution of the polymer sample. The polymer with broader PDI is easier to process because of its better flow behavior [4].
From the measurement of the intrinsic viscosity, the viscosity average molecular weight, \( M_\eta \), is defined as:

\[
M_\eta = \left( \frac{\sum n_i M_i^{\alpha+1}}{\sum n_i M_i} \right)^{\frac{1}{\alpha}}
\]  

(4)

where \( \alpha \) is the coefficient from the Mark-Houwink relationship:

\[
[\eta] = K M^\alpha
\]  

(5)

Equation 5 shows that when \( \alpha = -1 \), \( M_\eta = M_n \). When \( \alpha = 1 \), \( M_\eta = M_w \). Normally, \( \alpha \) is in the range between 0 and 1 depending on the polymer chain conformation, so \( M_\eta \) is smaller but closer to \( M_w \).

Figure 2.2 is an example of a Molecular weight distribution, showing the various mass averages.

![Figure 2.2](image)  

Figure 2.2  An example of a molecular weight distribution
The definitions of the average molecular weight can also be expressed as a continuous version:

\[ M_u = \frac{\int Mf(M)dM}{\int f(M)dM} \]

\[ M_w = \frac{\int M^2f(M)dM}{\int Mf(M)dM} \]

\[ M_z = \frac{\int M^3f(M)dM}{\int M^2f(M)dM} \]

(6)

Where \( f(M)dM \) is proportional to the number of polymer molecules with molecular weights between \( M \) and \( M+dM \).

Different techniques have been developed to measure the mass of polymers. Some commonly used methods are summarized in Table 1 [5] (adapted from Elias et al., Adv. Polym. Sci. 11, (1973), 111).

Table 1. Techniques commonly used for determining the polymer mass

<table>
<thead>
<tr>
<th></th>
<th>Method</th>
<th>Type *</th>
<th>Molecular Weight Range, g/mol</th>
<th>Mean Value Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Membrane osmometry</td>
<td>A</td>
<td>10^4-10^6</td>
<td>( M_n )</td>
</tr>
<tr>
<td>2.</td>
<td>Ebullioscopy (boiling point elevation)</td>
<td>A</td>
<td>&lt;10^4</td>
<td>( M_n )</td>
</tr>
<tr>
<td>3.</td>
<td>Cryoscopy (freezing point depression)</td>
<td>A</td>
<td>&lt;10^4</td>
<td>( M_n )</td>
</tr>
<tr>
<td>4.</td>
<td>Vapor Phase osmometry</td>
<td>A</td>
<td>&lt;10^5</td>
<td>( M_n )</td>
</tr>
<tr>
<td>5.</td>
<td>End group analysis</td>
<td>A</td>
<td>&lt;10^5</td>
<td>( M_n )</td>
</tr>
<tr>
<td>6.</td>
<td>Static light scattering</td>
<td>A</td>
<td>10^4-10^7</td>
<td>( M_w )</td>
</tr>
<tr>
<td>7.</td>
<td>Solution intrinsic viscosity</td>
<td>R</td>
<td>10^2-10^8</td>
<td>( M_\eta )</td>
</tr>
<tr>
<td>8.</td>
<td>Gel Permeation Chromatography</td>
<td>R</td>
<td>10^2-10^7</td>
<td>( M_w, M_n )</td>
</tr>
</tbody>
</table>
2.2.3 Viscosity

The viscosity of a fluid is defined as its resistance to gradual deformation by shear stress or tensile stress. It is due to the friction between neighboring particles in a fluid that are moving at different velocities.

![Fluid between a stationary plate and moving plate](image)

Figure 2.3 Fluid between a stationary plate and moving plate

For a fluid filling a space between two parallel plates as shows in Figure 2.3, the bottom plates does not move, and the upper layer slides in the y direction while keeping the distance between two plates constant. The fluid between the two plates generally moves faster near the upper layer and very slow near the bottom, as shown in Figure 2.3. Some stress is needed to overcome the friction between different layers of fluid and keep the fluid moving. The stress is defined as the force F per unit area A,
called the shear stress, $\sigma$

$$\sigma = \frac{F}{A} \quad \quad (7)$$

As shown in Equation 8, if the shear stress arising from the liquid flow is proportional to the local strain rate—the rate of change of its deformation over time, the fluid is viewed as Newtonian fluid.

$$\eta \frac{dv_y}{dx} = \sigma \quad \quad (8)$$

where $dv_y/dx$ is the velocity gradient, and $\eta$ is the viscosity of solution.

The diluted polymer and surfactant solutions involved in this work are viewed as Newtonian fluid.

Viscosity is another important characteristic in polymer or colloid solution, which provides the hydrodynamic information of solutions. In addition, the intrinsic of polymer solution can be related to the $M_w$ and conformation of polymer chains.

Adding polymer or surfactant molecules into solution generally increases the viscosity of the fluid due to the large differences in size between the polymer and solvent molecules. The viscosity of diluted polymer solution reflects its total resistance to flow. The resistance from the interaction between solvent molecules is the viscosity of pure solvent, $\eta_0$. There are also resistance between polymer molecules interaction and the interaction between polymers and solvents. The viscosity of the solution, $\eta$, represents the combination of these three effects. Normally, $\eta > \eta_0$ at same temperature. The ratio of the solution viscosity $\eta$ to the viscosity of $\eta_0$ is defined as relative viscosity $\eta_r$, which can be obtained approximately by measuring the time
required for a given volume of the two solutions to pass through a capillary.

\[ \eta_r = \frac{\eta}{\eta_0} \]  

(9)

The increased percentage of viscosity due to the dissolved polymer in solvent is defined as specific viscosity

\[ \eta_{sp} = \eta_r - 1 \]  

(10)

For most polymer solution, its specific viscosity increase with the increase of polymer concentration. Dividing \( \eta_{sp} \) to \( c \) allows reduced viscosity to be obtained

\[ \eta_{red} = \frac{\eta - \eta_0}{\eta_0 c} = [\eta] + k[\eta]^2 c + \ldots \]  

(11)

which is defined as the specific capacity of the polymer to increase relative viscosity.

To remove the viscosity effect from the interaction between polymer molecules, the solution has to be diluted infinitely. So the polymer chains are far from each other, and there is no inter-chain interaction. The viscosity behavior in this condition represents the resistance between the polymer and solvent molecules only. It is defined as intrinsic viscosity, as shown in \textbf{Equation 12}.

\[ [\eta] = \lim_{c \to 0} \eta_{red} \]  

(12)

Intrinsic viscosity is independent of polymer concentration. It was found that the intrinsic viscosity can be related to the average molecular weight of polymer when the temperature is constant. The relationship between \( M_w \) and intrinsic viscosity is known as Mark-Houwink equation

\[ [\eta] = KM_w^\alpha \]  

(13)

where \( K \) and Mark-Houwink(M-H) coefficient \( \alpha \) are constants.
The M-H coefficient $\alpha$ is related to the polymer chain conformation. Table 2 shows the relationship between M-H coefficient and polymer chain conformation [6].

Table 2. Mark-Houwink coefficients for different chain conformations

<table>
<thead>
<tr>
<th>Polymer chain conformation</th>
<th>Sphere</th>
<th>Random Coil</th>
<th>Random Coil (with excluded volume)</th>
<th>Rod</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-H coefficient</td>
<td>0</td>
<td>1/2</td>
<td>4/5</td>
<td>2</td>
</tr>
</tbody>
</table>

The intrinsic viscosity at $\theta$ condition can also be related to the radius of the hydrodynamic volume as shown in Equation 14 [7]

$$[\eta] = \frac{\Phi}{M} \left( \sqrt{6} \langle S^2 \rangle_0^{1/2} \right)^3$$

where $\Phi$ is Flory viscosity constant, depending on the chain architecture and the hydrodynamic interactions, and $\langle S^2 \rangle_0$ is the $\theta$ condition mean square radius of gyration which will be discussed later.

Viscosity is a temperature-dependence parameter. Generally, the liquid viscosity tends to decrease as the temperature increases, because the high temperature causes kinetic or thermal energy to increase and the molecules become more mobile. Arrhenius model is a commonly used to describe the relationship between temperature and viscosity of polymer solution [8], as shown in Equation 15.

$$\eta(T) = \eta_r e^{\frac{E}{R(T_r-T)}}$$

where $\eta_r$ is the viscosity at the reference temperature $T_r$, $E$ is the activation energy, and $R$ is the ideal gas constant.

The commonly used method to determine the viscosity of solution is measuring
the pressure drop across a capillary through which a polymer solution flows through. If the flow is slow and therefore laminar, the viscosity of fluid along the length \( l \) of the capillary can be determined based on the Poiseuille’s law:

\[
\eta = \frac{\pi r^4 p}{8 Q l}
\]

where \( r \) is the radius of the capillary, \( p \) is the pressure drop along the capillary, and \( Q \) is the flow rate of solution. The pressure difference can be generated by a pump or just by gravity.

2.2.4 Polymer chain conformations and dimensions

While the main chain of most polymers is long, most polymer chains are not fully stretched, but twist to different conformations as shown in Figure 2.4. The conformation of polymer chains depends on the chain structure, degree of polymerization and the solvent conditions.

![Figure 2.4 Types of polymer chain conformations](image-url)

- Full stretched contour length
- Random coil
- Sphere like
- Rod like
Ideal polymer chain is a good start to study the conformation of polymer chains in solution. It is defined as a linear, flexible polymer chain without excluded volume. In this case, one end of the polymer chain can go any directions without restrictions, while the other end of the polymer chain is fixed at the origin of a coordinate system. This random walk leads to the random coil conformation of ideal polymer chain.

The mean-square end-to-end distance is a common used parameter describing the size of this random coil. For an ideal polymer chain (i.e., without a fixed bond angle or rotameric states), the probability distribution of the end-to-end length in spherical coordinates is

\[
w(r) = 4\pi r^2 \left( \frac{3}{2nl^2 \pi^{1/2}} \right)^3 \exp\left(- \frac{3r}{2nl^2}\right)^2
\]

where \( n \) is the number of monomers, \( l \) is the monomer-to-monomer length and \( r \) is the end-to-end length of polymer chain [9].

Then, the mean square end-to-end distance is defined as

\[
\langle r^2 \rangle = \int_0^\infty r^2 w(r) dr
\]

For the ideal polymer chain (Gaussian chain),

\[
\langle r^2 \rangle = nl^2
\]

The angle between the valence bonds is random in the ideal random coil model. However, the C-C bond angle, \( \theta \), is fixed in real polymer chains. Then, in the long chain limit (\( n \gg 1 \)), the mean-square end-to-end distance [10] is rewritten as:

\[
\langle r^2 \rangle = nl^2 \frac{1 + \cos \theta}{1 - \cos \theta}
\]
For branching polymers, one polymer chain may have several different ends; and the close ring polymers may not have an end. In addition, the mean square end-to-end distance cannot be measured directly in the experiment. It becomes less meaningful to use the mean square end-to-end distance to describe the polymer chain conformation.

An alternative, the root-mean-square radius of gyration, \( R_g \), is more useful to represent the average size of polymer chain. As shown in Figure 2.5, \( R_g \) is defined as the weight average distance from the center of mass to each component of polymer chains. \( R_g \) is more related to the polymer chain structure based on its definition, and can be obtained directly from the multi-angle light scattering.

\[
R_g^2 = \frac{\sum m_i r_i^2}{\sum m_i}
\]

Figure 2.5  Definition of radius of gyration

where \( m_i \) is the mass of each component and \( r_i \) is the distance from the center of mass to component \( i \).

As shown in Equation 21, for ideal random coil, the mean square radius of
gyration and the mean square end-to-end length can be related by an equation derived by Debye and separately, Stockmayer and Zimm[11].

\[ \langle R_g^2 \rangle = \frac{nl^2}{6} = \frac{\langle r^2 \rangle}{6} \]  

(21)

Contour length \( L \) and persistent length \( L_p \) are commonly used parameters to characterize the dimensions of flexible polymers. Contour length is defined as the fully stretch length between the ends of the polymer chain. The persistence length measures the flexibility of polymer chains, and is defined as the length over which correlations in the direction of the tangent are lost. The persistence length is a basic mechanical property quantifying the stiffness of a polymer chain.

The mean square end-to-end length, contour length and persistence length can also be related in an equation

\[ \langle r^2 \rangle = 2L_pL \left[ 1 - \frac{L_p}{L} \left( 1 - e^{-L/L_p} \right) \right] \]  

(22)

In the rod limit \( (L_p \gg L) \), the chain is either rigid or very short

\[ \langle r^2 \rangle = L^2 \left[ 1 - \frac{L/L_p}{3} + \frac{(L/L_p)^2}{12} - \cdots \right] \]  

(23)

If \( L/L_p \sim 0 \), \( <r^2> = L^2 \), in the coil limit \( (L_p << L) \),

\[ <r^2> = 2LL_p \]  

(24)

Landau and Lifschitz [12] further related \( L \) and \( L_p \) to more experimental useful \( R_g \) by Equation 25

\[ \langle R_g^2 \rangle = L_p^2 \left[ \frac{2L_p^2}{L^2} \left( \frac{L}{L_p} - 1 + e^{-L/L_p} \right) - 1 + \frac{L}{3L_p} \right] \]  

(25)
For coil chain (L_p << L), only lower order term is kept, and
\[
\langle R_g^2 \rangle = \frac{L_p L}{3} = \frac{\langle r^2 \rangle}{6} \tag{26}
\]

For rod limit (L/L_p << 1),
\[
\langle R_g^2 \rangle = \frac{L^2}{12} \left[ 1 - \frac{L/L_p}{5} + \frac{(L/L_p)^2}{30} - \ldots \right] \tag{27}
\]

If L/L_p~0,
\[
\langle R_g^2 \rangle = \frac{\langle r^2 \rangle}{12} \tag{28}
\]

Another difference between the ideal chain and real polymer chain is different monomers of polymer chains cannot occupy the same space. It is pictured by a self-avoiding model, in which, the moving end of polymer chain in the random walk model cannot visit the sites which have been occupied by parts of itself or any other polymer chain. Therefore, the dimension of the real polymer chain is bigger than that of ideal chain. This is called excluded volume of the polymer chain. Figure 2.6 is a simple example to compute the total excluded volume between two hard spheres.

\[
EV = \frac{4}{3} \pi (2R)^3
\]

Figure 2.6  The excluded volume between two hard spheres
In polymer solutions, if the inter-particle attractive force is canceled by repulsive force, the polymer is in its unperturbed condition. And this is called $\theta$ condition. According to Van’t Hoff law for ideal solution

$$\Pi = \frac{cRT}{M}$$

(29)

where $\Pi$ is the osmotic pressure of the solution, $M$ is the mass of the polymer chain, $R$ is the gas constant, and $T$ is the absolute temperature.

For polymer solutions with excluded volume, Equation 29 can be expanded by virial expansion to generalize the Van’t Hoff law for real polymer solution.

$$\Pi = cRT\left(\frac{1}{M} + A_2 c + A_3 c^2 \cdots \right)$$

(30)

Here, $A_2$ and $A_3$ are called (osmotic) virial coefficients. They represent the deviation between the ideal solution and real solution. $A_2$ depends only on the two-body interaction between particles, and $A_3$ considers the volume mutually excluded in a three particle collision. In good solvent ($A_2 > 0$), the polymer chains repulse each other and expand itself because the solvent is energetically favorable for polymer-solvent interaction. When $A_2$ is negative, the intermolecular attraction is dominant in the solution, the polymer chains tend to aggregate and shrink, and the solvent quality is poor. If the attraction effect from poor solvent completely cancels the effect of excluded volume expansion, there is no interaction inside the solution. The polymer solution is in its $\theta$ condition ($A_2 = 0$). $A_3$ is only considered when the concentration of polymer is very high.

$\theta$ condition is close to but not the ideal condition. There is no thermal effect in
ideal solution. The ideal behavior of ideal solution exhibits at any temperature, while the theta condition is a temperature-dependent state.

2.2.5 Thermodynamics of polymer solutions

2.2.5.1 Dissolution of polymers

The dissolution of polymers is a complicated and slow process compared with the dissolution of small molecules. Because of the high molecular weight, the diffusion rate of polymers is much smaller than that of solvent molecules. The first step of dissolution is the small solvent molecules diffuse into polymer chains, and increase the volume of polymer matrix. After the swelling process of polymers, the solvated polymer molecules disperse into a solution to finish its dissolution. For highly cross-linked polymers, the polymer-polymer interaction is stronger than the polymer-solvent interaction. Thus, the dissolution of this kind polymer ends at first step as a swollen gel.

![Diagram of two-step dissolution of polymers](image)

Figure 2.7 Two-step dissolution of polymers
The condition for spontaneous dissolution is the decrease of mixing Gibbs energy (ΔG), as shown in Equation 31,

\[
\Delta G = \Delta H - T\Delta S < 0
\]

(31)

where T is the temperature, ΔH is the enthalpy of mixing and ΔS is the change of entropy.

Usually, the change of entropy is positive during the dissolution process because of the dispersing of solutes. The change of Gibbs energy depends on the mixing enthalpy. The mixing enthalpy is related to the polarity index of two mixing components. The closer is the two components’ polarity index, the smaller is the mixing enthalpy change. For example, when the polar polymer dissolved in a polar solvent, the dissolution is an exothermic process (ΔH<0) because of the strong polymer-solvent interaction. Thus the mixing of two components happens spontaneously.

2.2.5.2 Flory-Huggins Mean-Field Theory and Phase Behavior

Based on the Gibbs-Helmholtz Equation 31, the solvent quality for a given polymer can be changed by changing its temperature. Higher temperature normally is more favorable for dissolution. As the temperature changes, it is possible to draw a phase boundary curve on a temperature-composition plane, which can be viewed as the phase diagram for the binary system. The phase separation happens when the temperature crosses this phase boundary for a specific components ratio. There are different types of binary phase diagram [13] as shown in Figure 2.8. Flory-Huggins
mean-field theory is proposed to illustrate the thermodynamics properties behind these scenes.

![Figure 2.8 Different types of binary phase diagram](image)

(Adapted from Honeycutt et al., *Trends in Polymer Science* 2 (1994), 8)

**Flory-Huggins Mean-Field Theory**

Flory-Huggins theory uses the lattice model to arrange the polymer chain molecules and solvent molecules. **Figure 2.9** is a two-dimensional version of the lattice model. This lattice contains n sites. Each lattice site contains either a solvent molecule or a repeating unit of the polymer chain (assuming the repeating unit and the solvent molecule occupy the same space), so that \( n_{\text{total}} = n_s + n_p N \), where \( n_s \)
and \( n_p \) are the number of solvent molecules and repeating unit of polymer chains, respectively, and \( N \) is the degree of polymerization.

![Figure 2.9 Lattice model for polymer solution](image)

(Adapted from Enders et al, Polymers 4 (2012), 72)

The total number of microstates, \( \Omega \), in this model can be calculated assuming the polymer is a monodisperse homopolymer. Based on the Boltzmann law,

\[
S = k_B \ln \Omega
\]  

(32)

where \( k_B \) is the Boltzmann constant and \( S \) is the entropy.

The entropy change of mixing polymer and solvent molecules is obtained as

\[
-\Delta S_m / (k_B n_{total}) = \frac{\phi}{N} \ln \phi + (1 - \phi) \ln(1 - \phi)
\]  

(33)

where \( \phi \) and \( 1-\phi \) are the volume fractions of polymer and solvent molecules in solution

\[
\phi = \frac{n_p N}{n_{total}}, \quad 1 - \phi = \frac{n_s}{n_{total}}
\]  

(34)
The free energy can be obtained by \( \Delta G = \Delta H - T\Delta S \),

\[
\frac{\Delta G}{n_{\text{total}}k_B T} = \frac{\phi}{N} \ln \phi + (1-\phi)\ln(1-\phi) + \chi \phi(1-\phi)
\]

(35)

Similarly, the enthalpy change of mixing for the polymer solution is given in terms of

Flory-Huggins parameter, \( \chi \)

\[
\frac{\Delta H}{(n_{\text{total}}k_B T)} = \chi \phi(1-\phi)
\]

(36)

\[
\chi = \frac{[U_{ps} - (U_{ss} + U_{pp})]}{K_BT}
\]

(37)

where \( \chi K_BT \) represents the energy change due to the mixing of a solvent molecule with polymer chain. \( U \) refers to the chemical potential determined from partial derivative of free energy with respect to the number of the specific component.

Although there are some limitations on Flory-Huggins model, such as it assumes polymer molecules are of same size, and ignores the volume change upon mixing and the rigidity of polymer chain, it is still a widely used model and has been successful in describing thermodynamics of polymer solutions because of its concise form and physical meaning.

**Phase behavior of polymer solutions**

As discussed before, the miscibility for specific multi-component system depends on the temperature and the ratio of different components in the solution. When the phase separation happens in the polymer solution, the two phases must coexist under equilibrium conditions at certain points. And the diffusion rates of polymer in high concentration phase and low concentration phase should also reach to equilibrium at
the same time. In other words, the chemical potentials of polymer in both phases are the same.

\[
\left. \frac{\partial \left( \frac{\Delta G_M}{n_{\text{total}}k_B T} \right)}{\partial \phi} \right|_1 = \left. \frac{\partial \left( \frac{\Delta G_M}{n_{\text{total}}k_B T} \right)}{\partial \phi} \right|_2
\]

(38)

Then, the coexistence curve/phase boundary for this binary system can be determined by tracing out the values at which \( \phi \) occurs for each value of \( T \).

Flory-Huggins interaction parameter, \( \chi \), is a temperature dependent parameter. When \( \chi \) decreases with temperature increases, for example, in a form \( \chi = A + B/T \), where \( A \) is negative and \( B \) is positive, the phase separation happens upon cooling. And the phase diagram exhibits an upper critical solution temperature (UCST). In contrast, the phase diagram shows the lower critical solution temperature when the phase separation occurs upon heating. In this case, the F-H interaction parameter increases with temperature, for example, in a form \( X = A + B/T \) where \( A \) is positive and \( B \) is negative[14].

UCST is more straightforward than LCST since most mixing processes are entropy driving, and increasing temperature is favorable for the increase of the mixing entropy. However, for phase diagrams with LCST, the mixing of two phases happens spontaneously below LCST, and the change of Gibbs free energy is negative during the mixing process. So the change of mixing entropy \( \Delta S = (dG/dT) < 0 \), which is in contrary to the law of entropy. Two physical origins have been found to be responsible for this. First, the strong associating interaction between two components may prevent random mixing, which is very common in the amines-water system[15]. The
compressibility effects in polymer-solvent system can also lead to an LCST [16].

There are also cases where F-H interaction parameter is not a monotonic function of temperature and may have a maximum and/or minimum value vs. T. This leads to more complex binary phase diagrams as shown in Figure 2.8.

A spinodal curve can also be determined when the second derivative of \( \Delta G_M/n_{total}k_B T \) is zero. Between the spinodal curve and coexistence curve, as shown in Figure 2.10, the binary system is stable against phase separation with respect to small fluctuation in composition or temperature. However, large perturbations lead to the destabilization and phase separation.

![Phase diagram with spinodal curves](image)
2.2.6 Water-soluble polymers

Water-soluble polymer contains a large number of hydrophilic groups (such as carboxyl, ether, hydroxyl or amine groups) on its polymer chain, so it can swell in water and then disperse to form a solution. Generally, the conformation of the polymer in the solution depends on the two kinds of interactions, 1) the interaction between the polymer chain and the solvent molecule; 2) the inter-chain interaction.

The conformation of polymer chains change a lot at different concentrations. The properties of polymer solution also have significant differences. Therefore, the discussion of the properties of polymer solution has to be limited in the specific concentration regime. To define the concentration regime of polymer solution is a complex issue. In the late 1970s, de Gennes [17] divided the polymer solution into three types: a dilute solution, semi-dilute solution and concentrated solution.

In the dilute solution, the polymer coils are dispersed and far from each other. There is no strong interaction between polymer chains, and the polymer chains mainly interact with solvent molecules. The thermodynamic properties of dilute solution are close to those of ideal solution. With the polymer concentration increasing to semi-dilute regime, the properties of polymer solution are dramatically different from those of dilute solutions. The overall chain motion is slow because the polymer chains are entangled, and the solutions become highly viscous. As the polymer concentration keeps increasing into the concentrated regime, the density of polymer chains in the solution becomes continuous and homogeneous. The properties change of the
polymer solution from dilute regime to concentrated regime represents the shift from the properties of single polymer chain to the multiple chains interaction.

Figure 2.11 Three polymer concentration regimes

This work only focuses on the properties of dilute polymer solutions, because it is in a thermodynamic equilibrium state, and can be described by thermodynamic parameters. The molecular weight distribution of the polymers, size of polymer chains and other structural parameters of polymers also can be obtained in dilute solutions.

2.2.7 Charged Polymers

2.2.7.1 Polyelectrolytes

Polyelectrolyte is a type of polymers with repeating net charge groups. Because its properties is similar to electrolyte (salt) and polymer (high molecular weight), it is being used widely as thickeners, dispersants, flocculation aids and so forth[18][19][20]. Unlike the neutral polymer, its polymer chain conformation largely depends on the ionic strength of solvent. As shown in Figure 2.12,
When the ionic strength of solvent is low, the polymer chain is in an expanded state because of the electrostatic repulsion from net charge groups on the polymer chain. However, with the addition of simple electrolyte, more and more ions diffuse into the coil chain of the polyelectrolyte, which screens the electrostatic repulsion. Thus the polymer chains collapse, and the viscosity of solution decreases. This is known as polyelectrolyte effect. Virial coefficients of polymer solutions also show abnormal change during this process. Extra attention has to be made to characterize the solution behavior of polyelectrolyte by light scattering and osmometry because of this.
2.2.7.2 Polyzwitterions

There is a special type of charged polymers, known as polyzwitterions or zwitterionic polymers, with both cationic groups and ionic groups on its polymer chain. Because of the electrostatic attraction between different charged groups on the polymer chain, the conformation of zwitterion polymers tend to shrink or form a crosslinking structure in water, which leads to its poor water solubility. Increasing ionic strength of its aqueous solution improves the solubility of polyzwitterions significantly. The added salts shield the electrostatic attraction, break up the crosslinking structure, and therefore, the polymer chain expands in solution. The hydrodynamic volume and viscosity of the polyzwitterions increase with the ionic strength goes up, which is totally contrary to the behavior of polyelectrolyte. This is known as anti-polyelectrolyte effect of polyzwitterions [21]. The solution behavior of polyzwitterions also depend on the chemical structure, composition and solvent conditions [22].

2.2.8 Polymerization

Polymerization is a process, in which relatively smaller monomers chemically combine together to form a chainlike big molecules called polymers. The polymerization process can be grouped into step-growth and chain-growth polymerization based on the reaction mechanism. In a step-growth polymerization,
the multi-functional monomers react to form dimers first, then trimers, and the chains get larger as the reaction progresses. For chain-growth polymerization, the unsaturated monomers attach onto the active site of a growing polymer chain. The addition of unsaturated monomers regenerates the active site for polymer chain growing, until the reaction is terminated. Therefore, chain-growth polymerization produces polymers of high molecular weight in early reactions, while the larger polymers would be produced at the end of the step-growth reactions. The polymerization mechanism involved in this work is free radical chain-growth polymerization.

Free radical polymerization is one of the most important polymerization method in polymer chemistry. About 45% of the manufactured plastic materials and 40% of synthetic rubber are obtained by free radical polymerization processes [23]. In an ideal situation, the free radical polymerization includes three steps: chain initiation, chain propagation, and chain termination.

Chain initiation:  \( I \rightarrow 2R\cdot \)

\( R\cdot + M \rightarrow RM\cdot \)

Chain propagation: \( RM\cdot + M \rightarrow RM_2\cdot \)

\( RM_2\cdot + M \rightarrow RM_3\cdot \)

\( \cdots \cdots \)

\( RM_{n-1}\cdot + M \rightarrow RM_n\cdot \)

Chain termination: \( RM_n\cdot + RM \rightarrow P_{\text{dead}} \)
The initiator I dissemble into primary radicals $R^\cdot$ in the beginning. Subsequently, the $\pi$ bond of monomer $M$ is broken by the radical $R^\cdot$, which forms another bond with one of the electrons. Then the other unsaturated electron becomes a new active spot, and the whole molecule $RM^\cdot$ becomes a new radical. This new initiated monomer react with other monomers, and the polymer chains grow in the chain propagation steps. If two active chains meet each other during the chain propagation process, a dead polymer is formed, and the growing of polymer chain is terminated. The growth of polymer chains can also be terminated by chain transfer in free radical polymerization. Normally it is not a desired process because of the production of short chain polymers and high polydispersity.

2.3 Surfactants

2.3.1 Introduction

Surfactant is an amphiphilic compound which includes both hydrophobic and hydrophilic groups on its chain. Surfactant is active at a surface, and it is characterized by its tendency to absorb at surfaces and interfaces.

Based on the charge of the polar head group, the primary classification of surfactants includes anionic surfactants, cationic surfactants, neutral surfactant and zwitterionic surfactants. Anionic surfactants are the most commonly used surfactants among them, because of the ease and low cost of manufacture. Neutral surfactants are the second largest surfactant group. Most of them are compatible with other types of
surfactants, and the mixture of neutral surfactants with other surfactants are particularly useful to stabilize oil-in-water emulsions. Normally, cationic surfactants are not compatible with anionic surfactants. Mixing anionic and cationic surfactants would cause the precipitation. The main use of cationic surfactants relates to the in-situ modification of negatively charged surface like the surface of metals, minerals, plastics, etc [24]. Zwitterionic surfactants are used in cosmetic products because of its low skin irritation[25].

Surfactants have been widely used in industry mainly because the existence of surfactants can significantly reduce the surface/interfacial tension by their accumulating on the phase boundary.

Figure 2.13  The behavior of surfactants in aqueous solution
As shown in **Figure 2.13**, the hydrophilic part of the surfactant is attracted by water molecule in aqueous solution, while the hydrophobic part is repulsed by water molecule. To reach an equilibrium state, surfactant molecules will diffuse in the water and absorb at the interface between water and air. The hydrophobic group may extend out of the water phase, into air, while the hydrophilic group remains in the water. When the water-air phase boundary is covered by the surfactants, the energy required to expand the interface is reduced, so is the surface. The reduction of surface tension is directly proportional to the amount of surfactants. Similar processes also occur at other interfaces such as water-oil or solid-liquid interface [26].

As the increase of surfactant concentration in solution, water surface is eventually saturated to the absorption of surfactants, and the surface tension of solution does not change much after the saturation. More surfactants would lead to the formation of surfactant micelles which will be discussed next.

### 2.3.2 Critical micellization concentration (CMC)

The self-assembly of surfactant molecules is another fundamental property of surfactants. As discussed above, in aqueous solution, the surfactant unimers start to aggregate and form different structures after certain concentration. The common feature of these structures is that the non-polar/hydrophobic group of surfactants aggregate and form a nucleus, and the polar/hydrophilic group wrap up this hydrophobic nucleus and form a hydrophilic shell to reduce the free energy of the
In 1925, Mc Bain [27] first named this structure as micelle. The concentration at which the surfactant molecules start to form micelles is defined as critical micelle concentration (CMC). CMC is a vague range of small molecular weight surfactants, which however, becomes more and more well-defined as the increase of surfactants chain length [28]. Because of the formation of micelles, the surface tension does not change much after the CMC. Other physical and chemical properties of surfactant solutions like conductivity, osmotic pressure become discontinuous.

2.3.3 Micelle structures

The spherical micelle is one common structure of surfactant micelles. The structure of micelles depends on the geometry of surfactant molecules and solution conditions such as surfactant concentration, temperature, pH and ionic strength[29]. The surfactant micelles often grow from spherical structure to elongated rod-like structure with the increase of surfactant concentration[30]. Lamellar, Hexagonal structures can also be formed at higher concentrations. Temperature has similar effect on non-ionic surfactants[31]. The concept of critical packing parameter (CPP) provides geometric packing reasons for micelles structure.

\[
CPP = \frac{v}{l_{\text{max}}a}
\]  

where \(v\) is the volume of the hydrophobic chain of a surfactant molecules, \(a\) is the area of head group and \(l_{\text{max}}\) is the extended length of hydrophobic chain.

The relationship between CPP and the structure of micelles has been studied for
years[32], and the CPP of surfactants and their preferred micelle structures is shown in Figure 2.14

![Figure 2.14 CPP of surfactants and their preferred micelle structures](image)

(Adapted from Garti et al, Self-Assembled Supramolecular Architectures: Lyotropic Liquid Crystals, Wiley, 2012)

### 2.3.4 Factors related to CMC

Lots of factors may affect the CMC of surfactant. The effect of ionic and temperature on the CMC will be discussed in this part.

#### 2.3.4.1 Temperature effect on micellization

Temperature has different influence on the CMC of different surfactants. For oxyethylene-containing surfactant system which covers most of nonionic surfactants,
increasing temperature decreases the CMC of surfactants. The hydrophilicity of nonionic surfactants depends on the interaction between oxyethylene group and water solvent. Higher temperature weakens this interaction and causes the reduction in hydration of the hydrophilic oxyethylene group, which is unfavorable for the surfactant micellization [33].

The self-assembly structure of surfactant micelles also changes as a function of temperature, which is from spherical micelles, to elongated micelles, to bilayer structures and reversed micelles [34]. This is also due to the reduced hydrophilicity of surfactant molecules, and the polar groups have to pack closer at higher temperature. The aggregation number of nonionic surfactant micelles increases significantly with the increase of the temperature.

![Micelle Structure Diagram](image)

**Figure 2.15** The micelle structure of non-ionic surfactants with respect to the temperature and EO chain length

As **Figure 2.15** shows, the chain length effect on nonionic surfactant micelle structure is totally different from the temperature effect, because more oxyethylene
groups lead to a better hydrophilicity of surfactants. Also, long chain surfactants are more sensitive to the change of temperature than the ones with short chain[35].

Cloud point is another characteristic feature of polyoxyethylene-based non-ionic surfactant system. With the increase of temperature, the neutral surfactant solution may start to scatter light strongly after certain well-defined temperature. There is a transition in solution from surfactant-rich to surfactant-poor environment, and the precipitation of surfactants happens. The onset temperature of this phase separation is defined as the cloud point. Most nonionic surfactants are used below their cloud point. The higher is the cloud point, the wider is the application of the surfactant.

The solubility of ionic surfactants usually decreases a little at low temperature, and increases dramatically at high temperature. The onset temperature for the strongly increasing solubility is known as Kraft point, which is a characteristic feature for ionic surfactants. There is no micelle below the Kraft point because of the limitation of surfactants solubility. So, Kraft point is also known as the critical micelle temperature. There is a Kraft point in many ionic surfactants which is rarely observed in non-ionic surfactants.

The CMC of ionic surfactants is less sensitive to the change of temperature. Consider ionic surfactant SDS as an example, the total change of its CMC from 30 to 80 degrees is about 20%.

2.3.4.2 Ionic strength effect on micellization

Adding salt does not have much influence on the CMC of neutral surfactants.
However, it decreases the solubility/cloud point of non-ionic surfactants because the existence of salts is unfavorable for the formation of hydrogen bonds between surfactants and water molecule.

The response of ionic surfactants to the change of ionic strength is more significant. Several reports\cite{36}\cite{37} show that the addition of salt dramatically lowers the CMC of surfactants. High ionic strength screens the electrostatic repulsion between the surfactant molecules, which is favorable for the micellization process. In addition, the addition of salts typically raises the Kraft point of ionic surfactants.

2.3.5 Driving force of micellization

A popular proposal claims that the micellization is an entropy-driven process. Based on the Gibbs-Helmholtz equation, $G=H-TS$, the driving force of micelle formation at constant temperature can be viewed as the significant increase of entropy of the system. However, the process of micellization is from disorder to order. The random dispersed surfactant molecules aggregate to form well-organized micelles after the CMC, which conflicts with the principle of entropy increase. The concept of iceberg-water structure is introduced to overcome this issue.

It is well-known that the structure of liquid water is viewed as tetrahedral, which assumes that every water molecule forms hydrogen bonds with four adjacent molecules. When the surfactant is dissolved in the water, the non-polar group modifies the water structure in the direction of greater “crystallinity”. In other words,
the water molecules build a microscopic “iceberg” around it. As the surfactant molecules start to form micelles after CMC, the aggregation between the hydrophobic groups of surfactants destroys the microscopic ‘iceberg’ structure. And the entropy of the system increases during the micellization process.

### 2.3.5 Thermodynamic models for micellization

The surfactant micelles solution is in a thermodynamic equilibrium system. Different thermodynamic models have been proposed to describe the micelles formation. Most of them can be divided into two broad categories, mass-action law model and pseudo-phase separation model[38][39][40][41]. The Gibbs free energy and other thermodynamic parameters of micellization process can be related to the critical micelle concentration at fixed temperature and pressure based on these models.

#### a. Mass-action law model (MA model)

The mass-action law model assumes micelles and unimeric surfactants are in association-dissociation equilibrium, and the process is treated as a reversible chemical reaction.

For an anionic surfactant micelle $M_jA_{j-z}^{z+}$ with $j-z$ surfactant anions $A^-$ and $j$ counterions $M^+$, the micellization process can be expressed as below,

$$jM^+ + (j-z)A^- \leftrightarrow \left(M_jA_{j-z}^{-}\right)^{z^+}$$

(40)
Then, the equilibrium constant $K_{ma}$ is

$$K_{ma} = \frac{[(M^-)_{j-z}^{z+}]}{[A^-]^{j-z}[M^+]^j} \quad (41)$$

As the concentration of surfactants approaches to CMC,

$$[A^-] \approx [M^+] \approx CMC \quad (42)$$

For the equilibrium system with surfactant anions, counterions and the micelle, the Gibbs free energy of micellization process can be written as

$$\Delta G_{ma} = -\frac{RT}{j} \ln K_{ma} \quad (43)$$

Substituting $K_{ma}$ into Equation 43

$$\Delta G_{ma} = RT[\ln CMC + \left(\frac{j-z}{j}\right)\ln CMC] = RT \ln \text{cmc} \left(2 - \frac{z}{j}\right) \quad (44)$$

Other thermodynamic parameters like the change of enthalpy ($\Delta H$) and entropy ($\Delta S$) can be determined based on the Gibbs energy.

$$\Delta S_{ma} = -(2z/j)R \ln CMC - (2z/j)RT \left(\frac{\partial \ln \text{cmc}}{\partial T}\right) \quad (45)$$

$$\Delta H_{ma} = -(2z/j)RT^2 \left(\frac{\partial \ln \text{cmc}}{\partial T}\right) \quad (46)$$

b. Pseudo-phase separation model (PS model)

This model considers that micelles separate as a distinct phase at CMC, and the solution is formed of two pseudo-phases: the aqueous and the micelle phases. Above the CMC, the concentration of surfactants only affects the micelle concentration, and
the concentration of surfactant monomers in solution is always equal to the CMC.

For ionic surfactant

\[ jM^+ + jA^- = (MA)_j \] (47)

For non-ionic surfactant,

\[ jS = (S)_j \] (48)

where MA and S represent the new phase-micelles, j is the aggregation number of the micelle.

This model is simple to apply for experimental observation. The calculated Gibbs energy for the micellization of surfactants is similar like the one from Mass-action law model, as shown in Equation 49 and 50.

\[ \Delta G_{ps} = -\frac{1}{j} RT \ln \left( \frac{[(MA)_j]}{([M_+][A_-])^j} \right) \quad \text{for ionic surfactant} \] (49)

\[ \Delta G_{ps} = -\frac{1}{j} RT \ln \left( \frac{[(S)_j]}{[S]^j} \right) \quad \text{for non-ionic surfactant} \] (50)

At CMC, \([M_+] = [A_-] = \text{CMC}\) for ionic surfactants, and \([S] = \text{CMC}\) for nonionic surfactants. Then, the change of Gibbs energy, enthalpy and entropy of the micellization process for ionic surfactants are:

\[ \Delta G_{ps} = 2RT \ln \text{CMC} \] (51)

\[ \Delta S_{ps} = -2RT \left( \frac{\partial \ln \text{CMC}}{\partial T} \right) \] (52)

\[ \Delta H_{ps} = -2RT^{2} \left( \frac{\partial \ln \text{CMC}}{\partial T} \right) \] (53)
The $\Delta G_{ps}$, $\Delta H_{ps}$ and $\Delta S_{ps}$ of micellization for non-ionic surfactants are

$$\Delta G_{ps} = RT \ln CMC$$  \hspace{1cm} (54) \\

$$\Delta S_{ps} = -R \ln CMC - RT \left( \frac{\partial \ln CMC}{\partial T} \right)$$  \hspace{1cm} (55) \\

$$\Delta H_{ps} = -RT^2 \left( \frac{\partial \ln CMC}{\partial T} \right)$$  \hspace{1cm} (56) \\

Back to the Gibbs energy calculated from MA model, as in Equation 44. When $z=0$, j equivalent counter-ions are associated to the micelle, and the $\Delta G_{ma}$ calculated from MA model becomes same as the one for ionic surfactants from PS model:

$$\Delta G_{ma} = RT \ln CMC \left( 2 - \frac{z}{j} \right) = 2RT \ln CMC = \Delta G_{ps}$$  \hspace{1cm} (57) \\

Similarly, when $z=j$, no counter-ion is associated to the micelle, and the $\Delta G_{ma}$ calculated from MA model agrees with the one from PS model for non-ionic surfactants.

$$\Delta G_{ma} = RT \ln CMC \left( 2 - \frac{z}{j} \right) = RT \ln CMC = \Delta G_{ps}$$  \hspace{1cm} (58) \\

The ratio of counter-ions bound on the micelle surface to the concentration of counter-ions in the system is defined as the degree of counter-ion binding.

Once the CMC of surfactant is determined, both models are able to provide the thermodynamic information about the micellization process. Experimental results[42] show that $\Delta G$ is always negative, which indicates the formation of micelles is spontaneous.

Comparing with the phase separation model, the mass action law model is more
thermodynamically appropriate because the micelle formation is a reversible process. However, the calculations required for this model are very complicated, when the aggregation number is high or multiple components are involved in the micellization process. The phase separation model is easy to apply from a computational point of view, but it does not address the factors related to the aggregation number of micelles.

2.3.6 Surfactant-Polymer interactions

2.3.6.1 Critical aggregation concentration

Polymer-surfactant interaction has been studied extensively because of its wide application in different fields such as colloidal stability, emulsification, oil dispersion and rheology control [43][44][45][46]. One of the most significant features of surfactant is its ability to decrease the surface/interface tension between different interfaces. In the hypothetical case of the polymer-surfactant system shown in Figure 2.16, the surface tension of the surfactant only solution decreases rapidly at lower concentration, and then remains constant when the surfactant unimers aggregate to form micelles after the CMC. However, the existence of polymer in surfactant solution leads to one more inflection point on surface tension curve. This point is often termed as the critical aggregation concentration (CAC) of surfactant, at which the polymers start to associate with surfactants.
2.3.6.2 The driving force of polymer-surfactant interactions

The main driving forces for polymer/surfactant interaction are hydrophobic effect and electrostatic effect. Electrostatic effect is dominant if both surfactant and polymer are charged[47]. For polymer with hydrophobic segments, there is a hydrophobic attraction between the polymer and non-polar tail of the surfactant[48]. This provides thermodynamically favorable sites for surfactants to bind the polymer chains. Besides the electrostatic effect and hydrophobic effect, the hydrogen-bonding between Polyoxyethylene-containing non-ionic surfactants and polymers, and the ion-dipole association between dipole of the hydrophilic segment of the polymer and the ionic head group of the surfactant also affects the polymer/surfactant interaction[49]. The interaction between surfactant and polymer is very complicated. Normally, the aggregation between surfactants and polymers is due to the combination of all these interactions.
different types of interaction.

Take the interaction between polyethylene oxide (PEO) and sodium dodecyl sulfate (SDS) as an example, the partially protonated oxide group of PEO chain interacts with the ionic head group of SDS by Coulomb electrostatic attraction. The ~CH2~ groups of PEO tend to be bond within the aliphatic part of the micelles. In addition, there is an ion-dipole interaction between the headgroup of SDS and PEO chains.

2.3.6.3 Models/Structures of polymer-surfactant complex

Several scenarios have been provided to describe the aggregation between polymer and surfactant. Most of these models can be grouped into two groups: (a) attachment of individual surfactant unimers to the polymer chains because of the strongly cooperative association or binding energy between surfactants and polymers[50][51][52][53]; (b) micellization of surfactant in the vicinity of the polymer chain[54][55]. Both models have their own advantages. Binding theory is preferred for polymers with hydrophobic group. While for hydrophilic homopolymer, the micelle formation is more commonly used. And the pearl-necklace model, as shown in Figure 2.17 is a widely accepted scenario to describe the aggregate structure of the complex[56][57].
2.4 **Light scattering theory**

Light scattering can be viewed as the deflection of an incident light beam from a straight path by a scatterer, and it can be observed in all directions. Light is a form of electromagnetic wave with perpendicular electric and magnetic field. The scatterer is composed by atoms with positive charged nucleus and negative charged electrons. When the incident light penetrates through the atomic nucleus, the electromagnetic field causes the oscillation of surrounding electrons, and this becomes a new energy source that gives rise to scattered light. A completely homogeneous medium does not exhibit light scattering because the scattered waves cancels out each other. The irregularity in medium such as the difference of refractive index between polymers and solvents is required for light scattering[58].
In 1871, Rayleigh developed the Rayleigh scattering theory, while studying the light scattering of sunlight by particles in the air. He demonstrated that the scattering intensity was inversely proportional to the fourth power of the wavelength of incident light. In 1944, Debye measured the molecular weight of polymers in dilute solution based on the absolute light scattering intensity. Zimm proposed the well-known Zimm plot to characterize the properties of polymer in dilute solution in 1948. Since then, light scattering technique becomes a classic method to determine the mass, particle size and other structural parameters of polymer and colloid systems.

Rayleigh scattering requires that the particle size of the scatterer should be much smaller than the wavelength of the incident light. For example, the blue color of the sky is due to the Rayleigh scattering, which explains that the short-wavelength blue
light is scattered much more strongly than other long-wavelength lights by particles in the atmosphere. There are also other types of light scattering such as Mie scattering and Tyndall scattering which are very useful for studying the light scattering by large particles. The light scattering involved in this work is the Rayleigh scattering.

**Small particle in ideal solution**

For a vertically polarized laser beam, the incident light is an electromagnetic wave, and its time-dependent electric field can be written as:

\[ E_i = E_0 \cos(k_0 x - \omega_0 t) \]  \hspace{1cm} (59)

where \( E_0 \) is the amplitude of the electric field, \( k_0 = \frac{2\pi}{\lambda} \) is the propagation vector, \( \lambda \) is the wavelength in vacuum, and \( \omega_0 \) is the angular frequency.

In the Rayleigh scattering model shown in Figure 2.18, the incident light applied to the scatterer induces a dipole moment in that scatterer. The dipole oscillates with the frequency of the incident wave, and emits radiation as scattered light.

The magnitude of this oscillating dipole moment is proportional to the electric field, and this proportionality constant is the polarizability, \( \alpha \). The higher a scatter’s polarizability, the higher will be the magnitude of the dipole moment induced by incident light. The oscillating dipole moment defined as:

\[ p = \alpha E_i = \alpha E_0 \cos(k_0 x - \omega_0 t) \]  \hspace{1cm} (60)

Consider a scattered light at a distance \( r \) from the dipole to detector with angle \( \theta \) to dipole axis. The scattered light field is proportional to \((1/c^2)(d^2p/dt^2)\), where \( d^2p/dt^2 \) is the acceleration of the charge on the dipole moment and \( c \) is the speed of light. Also,
the electromagnetic field of the scattered light dies off as $1/r$. And the angle effect is considered by calculating the projection of the dipole moment on the observation direction. Combining all these effects, the electric field of the scattered light is written as:

$$E_s = \frac{(dp^2 / dt^2)(\sin \theta) / r}{c^2}$$  \hspace{1cm} (61)

The second derivative of the oscillating dipole with respect to time is:

$$\frac{dp^2}{dt^2} = \alpha E_0 w_0^2 \cos(k_x x - w_0 t)$$  \hspace{1cm} (62)

Substituting Equation 62 into Equation 63, the electric field of the scattered light is

$$E_s = \frac{(\alpha E_0 w_0^2)(\sin \theta)}{c^2 r} \cos(k_x x - w_0 t)$$  \hspace{1cm} (63)

The light scattering detectors measures the intensity of scattered light rather than the electric field. And the intensity of light scattering, $I$, is proportional to the square of electromagnetic field, $E$. So, the intensity is defined as:

$$I = \varepsilon_0 c \langle E^2 \rangle$$  \hspace{1cm} (64)

where $\varepsilon_0$ is the permittivity of light in vacuum and $\langle E \rangle$ is the field average over one vibration period.

And the scattered light intensity at distance $r$ and angle $\theta$ is

$$\frac{I_s}{I_0} = \frac{16\pi^4 \alpha^2 \sin^2 \theta}{\lambda_0^4 r^2}$$  \hspace{1cm} (65)

where $I_0 = E_0^2$.

The equation above is the Rayleigh equation for the light scattering intensity from
a single particle. For diluted ideal polymer solution with small particles, there is no interference between the scattered light from different parts on the particle. The light scattering intensity for $z$ moles particle in a dilute solution of volume $V$ can be written as

$$I_s = I_0 \frac{16\pi^4 \alpha^2 \sin^2 \theta z N_A}{\lambda_0^4 r^2 V}$$ (66)

In reality, it is difficult to measure the polarizability experimentally. Thus it is more convenient to use the relationship between refractive index and the polarizability of the solution. This relationship sets up a connection between the polymer properties and the light scattering intensity. Basically, the polarizability represents the difference of refractive index between the polymer and solvent. If the refractive index of polymer and solvent are the same, there is no polarizability and no light scattering. The polarizability of particles at concentration $c$ is

$$\alpha = \frac{ncV}{2\pi z N_A} \left( \frac{dn}{dc} \right)$$ (67)

Replacing $c$ by $zM/V$, where $M$ is the mass of particle, then

$$\alpha = \frac{nM}{2\pi N_A} \left( \frac{dn}{dc} \right)$$ (68)

Substituting Equation 68 into Equation 66, where $z/V$ is also replaced by $c/M$, and the light scattering intensity for ideal diluted solution is

$$\frac{I_s}{I_0} = \frac{16\pi^4 \sin^2 \theta n^2 \left( \frac{dn}{dc} \right)^2 cM}{\lambda_0^4 r^2 4\pi^2 N_A}$$ (69)

In a given light scattering experiment, $I_0$ and $r$ will be fixed. Multiplying the
Equation 69 by $r^2$, the dependence on the detectors distance from the scattering volume is eliminated. The excess Rayleigh ratio for ideal diluted solution is introduced as:

$$R_0 = \left( \frac{I_r}{I_i} \right) = KcM$$

where

$$K = \frac{4\pi^2 n^2 (dn/dc)^2 \sin^2 \theta}{\lambda_0^4 N_A}$$

is the optical constant depending on the $dn/dc$ of solvent, wavelength and the angle of the incident light.

**Small particles in non-ideal solution**

For non-ideal polymer solutions, the discussion above needs to be corrected by adding virial coefficients and concentration terms to the ideal results. As done with osmotic pressure, here

$$\frac{Kc}{R_0} = \frac{1}{M} + 2A_2c + 3A_3c^2 + \cdots$$

where $A_2$ and $A_3$ are virial coefficients.

Unlike the results from the osmotic pressure experiment, the molecule weight calculated from light scattering is weight average molecular weight, rather than the number average molecular weight from osmotic pressure.

**Light scattering by large particles**

There are two types of scattered light interference in the polymer solution, the interference from different polymer chains and the interference from the different parts of polymer chains. The interference from different molecules can be minimized
by using diluted solution. However, if the dimensions of the scattering particles increase to the order of the wavelength of incident light, the path difference for the scattered light from two points in the particle may be large enough to give an interference, which attenuates the light scattering intensity. A further improvement on classic light scattering theory is made to provide the information about the particle size and shape.

In order to quantify the dependence of the scattered light on the particle conformation, a new quantity is defined, the scattering form factor, $P(q)$.

$$P(q) = \frac{R_\theta}{R^{\theta}_{\theta}}$$

(72)

where $R_\theta$ is the actual scattering intensity at angle $\theta$, and $R^{\theta}_{\theta}$ is the scattering intensity without interference, $q$ is an angle dependent vector.

Form factor $P(q)$ is in the range between 0 and 1. There is no interference at zero scattering angle, and $P(0)$ is equal to 1. $P(q)$ is less than one for all other angles because the destructive interference can only attenuate the light scattering intensity. Now, for ideal solution with large particles, which does not consider the inter-chain interaction, the **Equation 71** is written as:

$$\frac{Kc}{R^\theta} = \frac{Kc}{P(\theta)R^{\theta}_{\theta}} = \frac{1}{M_pP(\theta)}$$

(73)

As for the non-ideal solution with large particles, the added virial coefficients and concentration terms change the **Equation 73** to:

$$\frac{Kc}{R^\theta} = \frac{1}{MP(q)} + 2A_2c + 3A_3c^2 + \cdots$$

(74)
To get the information about the polymer size and shape from Equation 74, it is necessary to get the expression for the form factor, $P(q)$. Different theoretical analysis on the expression of $P(q)$ have been made based on the Debye’s definition

$$P(q) = \sum_i \sum_j \frac{\sin qr_{ij}}{qr_{ij}}$$  \hspace{1cm} (75)

where $i$ and $j$ represent two elements along the polymer chain and the double summation is performed over all pairs of scattering element. The form factors for three polymer conformation of a simple geometry are summarized in the table below.

Table 3. $P(q)$ for polymers with different shapes (Adapted from Teraoka, I. Polymer solutions, Wiley-Interscience, New York, 2002)

<table>
<thead>
<tr>
<th>shape</th>
<th>$P(q)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere</td>
<td>$\left[ \frac{3}{x^3} (\sin x - x \cos x) \right]^2$, $x = 2\pi \frac{d}{\lambda} \sin \frac{\theta}{2}$</td>
</tr>
<tr>
<td>Coil</td>
<td>$\frac{2}{x^2} \left[ e^{-x} - (1 - x) \right]$, $x = \frac{8}{3} \pi^2 \sin^2 \frac{\theta}{2} \frac{\langle r^2 \rangle}{\lambda^2}$</td>
</tr>
<tr>
<td>Rod</td>
<td>$\frac{1}{x_0^2} \int_{x_0}^{x} \sin x \cdot dx - \left( \frac{\sin x}{x} \right)^2$, $x = 2\pi \frac{l}{\lambda} \sin \frac{\theta}{2}$</td>
</tr>
</tbody>
</table>

In the low concentration limit, when $qr_{ij} \ll 1$, $\sin(qr_{ij})$ can be expanded in a Taylor series, as shown in Equation 76:

$$\frac{\sin(qr_{ij})}{qr_{ij}} = 1 - \frac{1}{3!} \frac{1}{q r_{ij}} (qr_{ij})^3 + \cdots = 1 - \frac{(qr_{ij})^2}{6} + \cdots$$  \hspace{1cm} (76)

Hence,
\[ P(q) = \sum_i \sum_j \left[ 1 - \frac{(qr_j)^2}{6} + \cdots \right] = 1 - \frac{q^2}{3!} \left( \sum_i \sum_j r_j^2 \right) \]  \hspace{1cm} (77)

Since

\[ \left( \sum_i \sum_j r_j^2 \right) = \left( \sum_i \sum_j (r_i^2 + r_j^2) \right) = 2 \langle s^2 \rangle \]  \hspace{1cm} (78)

where \( <s^2>^{1/2} \) is the radius of gyration, Rg.

The form factor, P(q), becomes

\[ P(q) = 1 - \frac{q^2 \langle s^2 \rangle}{3} \]  \hspace{1cm} (79)

This expression applies to all shapes within the limitation of \( q^2 <s^2> \ll 1 \).

Substituting Equation 79 into Equation 74, the actual Zimm approximation for polymers in dilute concentration regime becomes:

\[ \frac{Kc}{R_g} = \frac{1}{M} \left( 1 + \frac{q^2 \langle s^2 \rangle}{3} \right) + 2A_2c \]  \hspace{1cm} (80)

A3 effect is only considered when the concentration of polymer is high. For polydisperse polymer solution, the average for \( R_g \) from Zimm approximation is the z-average.

Zimm approximation is extremely helpful to determine the \( M_w \), \( A_2 \), and \( <s^2>_z \) of polymers in diluted solution in multi-angle light scattering experiments with finite solution concentrations. To analyze the light scattering data by Zimm plot, two extrapolations are needed to eliminate the non-ideal effects. The extrapolation to zero concentration removes the effect of polymer chains interaction, and the extrapolation to zero angle remove the size-dependence effect.
The slope from the first extrapolation gives the information about the radius of gyration, $R_g$.

At $c=0$

$$\frac{d \left( \frac{Kc}{R_g} \right)}{dq^2} = \frac{\langle s^2 \rangle_s}{3M_w}$$

(81)

The slope from the second extrapolation gives the second virial coefficient $A_2$

At $q=0$,

$$\frac{d \left( \frac{Kc}{R_g} \right)}{dc} = 2A_2$$

(82)

The weight average molecular weight can be determined from the intercept of these two extrapolations. **Figure 2.19** shows the example of the Zimm plot method.
While Zimm plot is a powerful tool and widely used to characterize the properties of polymeric materials, there are some limitations about this method. For polymers with particle size less than 10nm, the light scattered equally at different angles and there is no angular dependence. So the $R_g$ cannot be determined in this situation. In addition, if the polymer is too big, a very steep extrapolation slope is expected, which leads to the error on the $M_w$. However, the $M_w$ can be estimated by the lowest angle. The assumption of $q^2<s^2> << 1$ no longer holds if the polymer is too big. Also, extra attention has to be paid to charged polymers because the big $A_2$ may lead to the underestimation of $M_w$. 
3. Techniques and detectors

3.1 Automatic Continuous Mixing (ACM)

ACM is a powerful technique to characterize the properties of materials during the equilibrium and quasi-equilibrium process. The most common use of the ACM is to characterize two-component system in terms of $M_w$, $[\eta]$, $R_g$, $A_2$, etc. The continuous data collected from ACM provides smooth polymer concentration gradient, improves the resolution of experiments, and offers more accurate and complete information on polymer characteristics[63].

The basic setup of ACM is shown in Figure 3.1. A programmable high performance liquid chromatography pump connected to a quaternary mixing unit, mixes and pumps the solution through the detector train including multi-angle light scattering detector, viscometer, RI, UV and others. The detectors are customizable depending on the requirements of the experiment. By automatically adjusting the flow ratio between solvent and stock polymer solution in quaternary mixing unit, ACM continuously dilute the polymer concentration to study its characteristics during the concentration gradient ramp.
ACM can also be used to study the effect of external stimuli (pH, ionic strength, etc.) on polymer chain conformation; multi-component interaction such as polymer and surfactant; as well as the dissolution kinetics of polymeric materials.

### 3.2 Multi-angle static light scattering

Multi-angle static light scattering (MALS) is the main light scattering technique involved in this work. As explained in the previous section, by measuring the average light scattering intensity as a function of scattering angle, the weight average molecular mass ($M_w$), the radius of gyration ($R_g$) and the second virial coefficient $A_2$ of polymer can be determined based on the well-known Zimm approximation

\[
\frac{Kc}{R_g} = \frac{1}{M} \left(1 + \frac{q^2 \left< s^2 \right>}{3} \right) + 2A_2 c
\]

where $K$ is an optical constant. For vertically polarized incident light:

\[
K = \frac{4\pi^2 n^2 (dn/dc)^2}{N_A \lambda^4}
\]
\( n \) is the refractive index of solvent, \( \lambda \) is the wavelength of the incident light in vacuum, \( dn/dc \) is the differential refractive index for the polymer in the given solvent, and \( q \) is the scattering wave vector given by
\[
q = (4\pi n / \lambda) \sin(\theta / 2)
\]
where \( \theta \) is the scattering angle.

This expression holds well with \( q^2 < s^2 > \ll 1 \) at low concentration limit.

The light scattering detector involved in this work is a BI-MwA multi-angle scattering photometer from Brookhaven Instrument, built on the original design from Reed’s research group, as shown in Figure 3.2. The polymer sample is flowed through a vertical cell with seven different detecting angles (35\(^\circ\), 50\(^\circ\), 75\(^\circ\), 90\(^\circ\), 105\(^\circ\), 130\(^\circ\), 145\(^\circ\)). The collected voltage data is converted to Rayleigh ratio by
Equation 83

\[ R_\theta = \left[ \frac{V_{\text{poly}}(\theta) - V_{\text{solvent}}(\theta)}{V_{\text{toluene}}(90^\circ) - V_{\text{dark}}(90^\circ)} \right] \times (I_{\text{ref,tol}})(F)(N_\theta) \]  

(83)

where \( V(\theta) \) is the collected voltage for polymer sample, solvent baseline, reference(toluene) and dark at angle \( \theta \), \( N(\theta) \) is a normalization factor, \( I_{\text{ref,tol}} \) is the known Rayleigh ratio of the reference, toluene, and \( F \) is an optical constant specific to the flow cell (\( F=0.94 \) for the Bi-MwA used).

For multi-angle light scattering detector, all the detectors from different angles need to respond the same way to sample solution. Normalization is an important step before starting the measurements by multi-angle light scattering detector. The light scattering signal from all the other angles are normalized to the signal of 90°. The flare light is minimized at the right angle, so it has best signal to noise ratio.

The normalization factor is calculated based on the Equation 84:

\[ N(\theta) = \frac{V_n(q_r) - V_s(q_r)}{V_n(q) - V_s(q)} \]  

(84)

where \( V_n(q_r) \) and \( V_s(q_r) \) are the light scattering signal (voltage) from the normalization solution and the pure solvent, respectively, at the scattering vector \( q_r \), which is a function of the reference angle \( \theta_r \); \( V_n(q) \) and \( V_s(q) \) are scattering voltages for the normalization solution and solvent, respectively, at angle \( \theta \).

The ideal normalization solution should be isotropic, like 20nm latex spheres in
Since they scatter uniformly in all directions, the detector efficiency and gain can be normalized with this procedure.

Since the light scattering detector measures the voltage signal rather than the absolute light scattering intensity directly, it is necessary to relate the voltage signal from detectors to the absolute Rayleigh ratio of the polymer sample. The common way to do that is to measure the voltage signal of a pure solvent with known Rayleigh light scattering ratio, which is Toluene in this case. $I_{\text{ref,tol}}$ in Equation 83 is the Rayleigh ratio of the reference Toluene.

### 3.3 Refractive index detector (RI)

The refractometer is a commonly used concentration detector. A glass cell is divided into sample cell and reference cell inside the RI, and the reference cell is filled with solvent. As shown in Figure 3.3, when the solvent flows through sample cell, the incident light beam is parallel to the refraction beam. However, when the polymer solution flows through the sample cell, there is a bending of the incident beam because of the difference of refractive index.
By measuring this change between the polymer solution and solvent, the concentration of the solution can be calculated by

\[ c(t) = CF \frac{V_{RI}(t) - V_{RI,base}}{dn / dc} \]

where CF is the refractometer calibration factor, \( V_{RI,base} \) is the baseline voltage of the refractometer when pure solvent is flowing, \( V_{RI}(t) \) is the voltages from RI at time \( t \) for solution and solvent baseline, \( dn/dc \) is the differential refractive index for the material.

As a concentration detector, RI has wide dynamic range, good sensitivity and high linearity with concentration. It can be used as long as there is a sizeable difference of \( dn/dc \) between solute and solvent.

The refractometers involved in this work are Waters 410 detector and Shimadzu
RID-10A detectors. The calibration factor is calculated based on the NaCl solutions of known refractive index (n) and concentrations.

3.4 Single capillary viscometer

A home-built single capillary viscometer is used in this work. It measures the voltage difference across the capillary which is proportional to the pressure drop across the capillary. Then the total viscosity of solutions can be determined based on the Poiseuille’s equation,

\[ \eta = \frac{\pi R^4 \Delta P}{8LQ} \]  

(86) 

where \( \Delta P \) is the pressure drop across the capillary of radius \( R \) and length \( L \), \( Q \) is the flow rate of the liquid.

Figure 3.4  Schematic of single capillary viscometer
The total solution viscosity is given by

\[ \eta = \eta_s \left[ 1 + [\eta]c + k_p[\eta]^2 c^2 \right] \]  

(87)

where \( \eta_s \) is the viscosity of the solvent, \([\eta]\) is the intrinsic viscosity, and \( k_p \) is related to the hydrodynamic interactions between polymer chains.

The specific viscosity which characterizes the fractional increase in viscosity due to the dissolved polymer in the solvent is defined as

\[ \eta_{sp} = (\eta - \eta_o) / \eta_o \]  

(88)

where \( \eta \) is the total viscosity, and \( \eta_o \) is the viscosity of solvent baseline.

The intrinsic viscosity which represents the intrinsic ability of a polymer to increase viscosity in a given fluid can be calculated based on the equation below

\[ [\eta] = \lim_{c \to 0} (\eta_{sp} / c) \]  

(89)

Single capillary is very sensitive to the temperature and pump pulses. Extra attention has to be paid on controlling the experimental conditions.

### 3.5 Electrical conductivity meter

When an ionic compound dissolved in polar solvent, its electrically charged ions enable the passage of current through the solution. Conductivity meter measure the ability of a current to flow through a trapped volume of solution between two plates on the conductance probe.
In practice, the conductivity (C) is calculated from the actual conductance (G) between the plates, multiplied by the cell constant (K).

\[ C = G \times \frac{L}{A} \]  

(90)

where C=conductivity (S/cm), G=Conductance (S), L=distance between plates (cm) and A=area of plates (cm2).

The conductivity of a solution highly depends on the temperature. It increases with increasing temperature. The influence of temperature on the conductivity[64] of a solution can be quantified as Equation 91.

\[ \sigma_T = \sigma_{T,\text{cal}} \left[ 1 + \alpha(T - T_{\text{cal}}) \right] \]  

(91)

where T is the temperature of the sample, T_{cal} is the calibration temperature, \( \sigma_T \) is the electrical conductivity at the temperature T, \( \sigma_{T,\text{cal}} \) is the electrical conductivity at the calibration temperature T_{cal}, and \( \alpha \) is the temperature compensation slope of the solution.

The electrical conductivity meter involved in this work is Jenway 3540 pH & Conductivity meter. The cell constant is 0.92 as shown on the probe.

### 3.6 Energy dispersive X-ray spectroscopy (EDS)

EDS is an analytical technique used for the elemental analysis on a sample. Each element has unique atomic structure, thus has unique set of peaks on its X-Ray
spectrum. As shown in Figure 3.5, when the high-energy electron/proton beam hit the sample, the incident beam may excite an electron in an inner shell, ejecting it from the shell. Then the electron from an outer, higher-energy shell fills the hole where the excited electron was, and releases the energy difference between the higher-energy and lower-energy shells in the form of X-ray. By measuring the number and energy of emitted characteristic X-rays, the elemental composition of specimen can be determined.
However, the Auger electrons may also be produced while releasing the energy between different energy shells, which leads to the error of measurement. As atom number increases, the influence from generated auger electrons decreases, so the EDS result is more reliable for heavy element analysis.

Energy Dispersive X-ray spectroscopy (EDS) integrated into Hitachi 3400 electron microscope is the one used in this work.

### 3.7 Simultaneous multiple sample light scattering (SMSLS)

SMSLS is a recently developed quantitative high-throughput technique\[65\] based on total light scattering intensity. It works similarly to the batch mode static light scattering, and all the measurements are made at 90° currently. The prototype SMSLS has eight independent light scattering cells, which allows monitoring eight different samples simultaneously. The SMSLS system can continuously collect the light scattering signal for months at a time or even longer. This allows SMSLS to study the time-dependent process like stability of polymer/colloidal solutions, the kinetics of aggregation gelation, and the degradation of materials.

A programmable temperature control system is recently built inside the SMSLS, which can adjust the temperature of each cell independently from room temperature to more than 100°C. This provides a new sensitive high-throughput platform to
characterize the thermal-dependent system, such as the phase transition process or the denaturation of proteins. The latest work [66] done by SMSLS correlates the activation energy of proteins to their stabilities for the first time, which represents a big advantage comparing with the traditional techniques.

Different neutral density filters can also be applied to scattering cells to reduce the light scattering intensity, which is very helpful for monitoring the phase separation or the aggregation process because of the very strong scattered light from those aggregates. Also, each scattering cell has its own step motor which can be used to control the convection energy of solution.

More improvements on this technique are ongoing to expand its application.
3.8 Automatic Continuous Online Monitoring Polymerization (ACOMP)

Automatic continuous online monitoring of polymerizations (ACOMP) is an analytical technique which helps understand the kinetics and mechanisms of polymerization, and optimize the polymerization process. It was first developed by Dr. Reed’s research group at Tulane University [67]. Lots of effort has been made to expand its applications over the past years.

The scheme below shows the basic set-up of the first generation ACOMP.
system. Several pumps and mixing chambers become the front-end of the ACOMP to extract and condition the polymer samples from the reactor. The back-end of the ACOMP is a combination of different detectors including MALS, UV, RI, VISC and etc. The basic idea of the ACOMP is a small stream from reactor is continuously withdrawn and automatically conditioned in the front end, then the diluted polymer sample is delivered to the back end to do all the characterizations. The existence of MALS allows the determination of molecular weight, particle size of polymers, as well as the Virial coefficient. The UV detector can be used to determine the consumption of monomers in the reactor. The differential refractometer reports the refractive index dn/dc of monomers and polymers, which is the must-have to analyze the data from MALS. Other information like the reduced viscosity, copolymer composition drift, the kinetics of reactions can also be obtained from the ACOMP.
Better knowledge of the reaction is gained with the information from the ACOMP, and thus, better process control and optimization of polymerization can be accessed. Ultimately, the goal of the ACOMP is to be used to monitor and provide full feedback control for full scale industrial reactors.
4. Results and analysis

4.1 Enhanced Surfactant Supramicellar Assembly by Hydrophobic Dopants

4.1.1 Introduction

The self-assembly of surfactants has been a fast developing research field both theoretically and technologically. Numerous works has studied about the micellization and premicellar aggregation process of surfactants using surface tension[68], NMR[69], fluorescence, light scattering, and other methods. Various factors such as the ionic strength of solution, the nature of hydrophobic or hydrophilic groups, and the presence of co-solutes have significant impacts on the self-assembly of surfactants around the CMC.

An increase in light scattering intensity (LS) as surfactant concentration approaches the CMC and decrease after the CMC was observed in 1955[70], LS vs the concentration of surfactants forms a well-defined ‘light scattering peak’ (LS peak). Early authors attributed LS peaks in SDS solutions to dodecanol/SDS adducts solubilized in micelles, that precipitated when solutions were diluted below the CMC[71]. Dodecanol is a native residue impurity left inside SDS due to the hydrolysis of SDS. Other authors also ascribed the phenomenon to impurities[72][73]. A diminution of the peak in time was observed[74], whereas others[75] found
no peak in fresh solutions. Others found LS peaks for purified surfactant, and reported it unchanging in time [76], and attributed them to large pre-micellar aggregates. Strong effects of low dodecanol levels on surfactant film draining properties were also found [77]. An extensive study of micellar solubilization of hydrocarbons considered the micelles in the LS peak regime to be rodlike and then to become globular at higher concentrations [78].

There have been numerous publications concerning surfactant/alcohol systems in general [79][80][81][82][83]. The properties of nanoemulsions produced by the Phase Inversion Concentration method have some similarity to those of dodecanol-doped SDS. Such nanoemulsions are not thermodynamically stable, but, due to their initial small droplet size and low polydispersity, they can remain kinetically stable for a long period [84][85][86].

Data herein confirm the impurity origin of LS peaks and that they are not due merely to impurity release near the CMC, rather, they correspond to long-lived metastable supramolecular surfactant assemblies much more massive than impurity-free micelles. These assemblies have reproducible characterizing features which form the basis of a simple model here. The experimental approach may prove useful for testing loading of impurities by micelles and other encapsulation agents, such as those used to scavenge oil after oil spills.
Dodecanol (D) and dodecane were used as impurities and are termed ‘dopants’, since LS peaks occur at very low ratio of the mass of dodecanol to the mass of SDS.

Earlier work lacked good LS peak resolution and peaks were first assumed due to release of impurities as micelles disappeared near the CMC, and were later thought due to particles formed from the adduct \( \text{LOH}\text{2} \text{SDS} \). That work found a linear LS decrease to solvent baseline scattering (SBS) at finite \( C_{\text{SDS}} \), termed \( C_e \), independent of dopant loading. The unmoving \( C_e \) was explained via the adduct solubility \( [D][\text{DS}]^2[\text{Na}^+]^2 \sim 10^{-18} \) and its much stronger dependence on \([\text{SDS}]\) than on \([D]\). The authors of that work admitted that the small changes in \( C_e \) calculable from the solubility product could easily be masked within the experimental error of their LS peak measurements.

The main goal of this work is to study the interaction between surfactant and hydrophobic dopant, and develop a model to explain the mechanism behind this unknown light scattering peak. Here, high resolution LS peaks show considerable change in \( C_e \) with dopant loading, which, together with other peak features, suggest the SDS/Dodecanol structures are dynamic ‘supramicellar assemblies’, possibly resembling closed-ring wormlike micelles.
4.1.2 Materials and Methods

Anionic surfactant sodium dodecyl sulfate (SDS) (A.C.S. reagent, 99+% ) and cationic surfactant dodecyltrimethyl ammonium bromide (DTAB A.C.S. reagent, 98+% ) were used as received form from Sigma-Aldrich. Dodecanol (>98%, A.C.S. reagent grade) was added into surfactant solutions well above the CMC as hydrophobic dopants. All doped surfactant solutions were stirred overnight at T=25°C. The doping level is defined as

\[ R = \frac{\text{mass of dodecanol}}{\text{mass of SDS}} \]

Deionized and filtered water (Purelab® Ultra Laboratory Water Purification System) was used through the experiments. All the solutions were filtered with 0.45mm Millex-GS Millipore membrane filter.

While Automatic continuous mixing (ACM) offers different approaches to characterize the properties of solution, it is used to monitor the behavior of SDS solutions by providing continuous gradients of SDS concentration, measured by light scattering, viscosity, and refractive index detectors in this work.

The ACM experiments here are grouped into two types.

(i) Increasing the concentration of surfactant with different doping levels. This allows the exploration of the dopant’s effect on surfactant solution behavior;

(ii) Increasing the concentration of surfactant with same doping levels in different
ionic strength solution. This allows the monitoring of the ionic strength’s effect on the interaction between surfactant and hydrophobic dopant.

The technique, introduced in previous work[87][88], used a programmable Shimadzu HPLC pump, connected to a two-line mixing unit to pump the solution, at 1mL/min, through a custom-built single-capillary viscometer, multiangle light scattering detector (LS, BI-MwA, Brookhaven Corp.), and a refractometer (RI, Waters) while continuously varying concentration of surfactant from 0 to 9mg/ml. An additional 0.45μm inline frit filter was used before the detectors to eliminate the large impurities.

The BI-MwA had a vertically polarized 660 nm incident laser beam and was set to smooth data in five-point continuous swaths while collecting scattering data at 2s intervals.

Continuously collected raw data were used to compute concentration of each species and different relevant physical quantities. The RI data yielded the concentration of surfactant as explained in chapter three. A weak linear dependence on [NaCl] was found for refractive index increments dn/dc of SDS (using a Shimadzu RI-10 refractometer)

\[
dn/dc \text{ (cm}^3/\text{g}) = 0.1225 - 2.67 \times 10^{-5} [\text{NaCl}] (mM), \\
0 \leq [\text{NaCl}] \leq 200 \text{mM}
\]
Multiangle static light scattering data analysis was carried out with the representation of Zimm in the low q limit for dilute solutions, applicable within the approximation \[ 1 > \frac{q^2 <S^2>_z}{3} , \]

\[
\frac{Kc}{I_R(q,c)} = \frac{1}{M_w} \left( 1 + \frac{q^2 <S^2>_z}{3} \right) + 2A_2c
\]

where \( q=(4\pi n/\lambda)\sin(\theta/2) \), \( M_w \) is the scatterers’ weight average molar mass, \( A_2 \) is the second virial coefficient, \( \theta \) is the scattering angle, \( n \) is the refractive index of solvent, \( \lambda \) is the wavelength of incident light and \( K \) for vertically polarized incident light is

\[
K = \frac{4\pi^2 n^2 (dn/dc)^2}{N_A\lambda^2}
\]

c is the scattering species concentration, and \( I_R(q,c) \) is the excess Rayleigh scattering ratio.

At [NaCl]=0, \( K=8.75\times10^{-8} \text{ Mole-cm}^2/\text{g}^2 \) for SDS. \( I_R(q,c) \) was determined via calibration of light scattering voltages via the known scattering of toluene at 660nm, and 25°C of \( I_{R,\text{toluene}}=1.19\times10^{-5} \text{ cm}^{-1} \).

Elemental analysis of precipitate from dopant-loaded SDS micelles was done by Energy Dispersive X-ray spectroscopy (EDS) integrated into Hitachi 3400 electron microscope. The quantities and qualities of the various components are determined
by analyzing the characteristic X-rays emitted from the precipitated specimen

Jenway 3540 pH & Conductivity meter is used to determine the CMC of surfactant. The cell constant is 0.92 as shown on the probe.

DLS measurements were made using a Brookhaven 90Plus particle size analyzer (90°, λ= 660nm) on stock doped SDS solution at different concentrations, in order to eliminate the effect of flow and mixing from ACM.

4.1.3 Results and Discussion

Micelles without dopant

As mentioned before, there is an unknown light scattering maxima around the CMC of dopant-free SDS in Figure 4.1, indicating the formation of big structures. The light scattering intensity returns to normal at higher concentrations of SDS. The discrete points in the figure are conductivity data which are used to determine the CMC of SDS.
Table 4 shows LS analysis for dopant-free SDS micelles for various ionic strengths (IS) for LS above the CMC and LS peak region. Micellar masses agree with previous literature[89][90] and are not strongly dependent on IS, whereas $A_2$ and CMC decrease by an order of magnitude as IS increases. $A_2$ vs IS has been quantified in terms of electrostatic excluded volume[91].

The later discussion shows that the undoped SDS displayed LS peaks due to residual dodecanol in the stock SDS. By using the dependence of $I_R$ discussed below,
it was determined that the residual amount of dodecanol in the stock SDS is approximately $R=5.5 \times 10^{-4}$. The CMC determined by conductivity closely follow the concentration of SDS doped micelles at the LS peak maximum for the tiny value of $R=5.5 \times 10^{-4}$.

Table 4. Undoped micelle properties

<table>
<thead>
<tr>
<th>[NaCl] (mM)</th>
<th>$M_0$ (g/mole)</th>
<th>$A_2$ (cm$^3$-mole/g$^2$)</th>
<th>$CmC^*$ (g/cm$^3$)</th>
<th>$C_{SDS}$ @ LS peak max (g/cm$^3$)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>18,100</td>
<td>4.50x10^{-3}</td>
<td>2.32x10^{-3}</td>
<td>2.35x10^{-3}</td>
</tr>
<tr>
<td>1</td>
<td>21,900</td>
<td>2.01x10^{-3}</td>
<td>2.22x10^{-3}</td>
<td>2.07x10^{-3}</td>
</tr>
<tr>
<td>10</td>
<td>21,600</td>
<td>2.25x10^{-3}</td>
<td>1.43x10^{-3}</td>
<td>1.38x10^{-3}</td>
</tr>
<tr>
<td>100</td>
<td>26,400</td>
<td>0.50x10^{-3}</td>
<td>N/A</td>
<td>0.11x10^{-3}</td>
</tr>
</tbody>
</table>

* by conductivity

** from peak in undoped stock SDS, estimated to have residual dodecanol of $R=5.5 \times 10^{-4}$

**Doped micelles: effects of loading and ionic strength**

**Figure 4.2** shows LS peaks for various doping level, $R$, at [NaCl] = 0. The peaks’ shapes and structure are similar to **Figure 4.1**. The SDS concentration at the peaks’ maximum, $C_p$, increases slightly as loading increases. Peaks are not
superposable onto each other by changes in x and y scale. The inset shows how the peak height $I_{R,max}$ scales linearly with $R$; $I_{R,max}(\text{cm}^{-1}) = 0.0167R$. This linear relationship can be used to estimate the residue impurity level of surfactant, even if it is below 0.1%. For the stock SDS $I_{R,max}=9\times10^{-6}\text{cm}^{-1}$ leading to the estimate that $R=5.5\times10^{-4}$ in the stock SDS. When there are many SDS micelles formed above the LS peak region, the light scattering behavior is less or not affected by doping. $M_w$ with dopant is slightly larger and $A_2$ slightly lower than for undoped micelles.

![Figure 4.2 $I_R$ vs. $C_{SDS}$ for various $R$ for SDS in water](image)

Figure 4.2 $I_R$ vs. $C_{SDS}$ for various $R$ for SDS in water
Large LS peaks for SDS/Dodecanol solutions of varying ionic strength and fixed R=0.033 are shown in Figure 4.3. The LS peak is large even at high IS where it seems to be almost negligible. Nonetheless, LS even at 100mM is about ten times higher than the scattering above the LS peak concentration (inset). The position of light scattering peak at different ionic strength is close to the CMC of SDS determined by the conductivity. This confirms that the LS peak of doped SDS solution is a CMC related phenomenon.

Figure 4.3  \( I_R \) vs \( C_{SDS} \) for R=0.033 and various [NaCl]
As striking as the LS peak amplitudes is the regularity of their structure and how they scale downwards as IS increases. Peak amplitude decreases while the rising slope from low $C_{SDS}$ to the peak remains approximately constant. Negative LS slopes after the peak are also similar. $C_p$ is near CMC. $C_e$, the concentration at which the peak ends and drops to the solvent baseline scattering, is only weakly dependent on IS and CMC at fixed $R$. This high regularity of LS peak at different ionic strength provides an opportunity to develop a model to quantity the relevant physical properties.

Figure 4.4 shows the ‘anatomy’ of the LS peak, characterized by several main parameters: the LS maximum, $I_{R,\text{max}}$, $C_{SDS}$ at which it occurs, $C_p$, the concentration at which the peak begins during dilution, $C_b$, the concentration at which the peak ends and drops to the solvent baseline scattering, $C_e$, and an inflection point $C_i$. The ‘dilution line’ from $I_{R,\text{max}}$ to zero at $C_{SDS}=0$ is expected for large particles below $C_p$ if they were simply diluted after they appear and had no solubility or dynamic surfactant properties of their own.
This first, simple model posits three SDS components: Monomeric (free) SDS, SDS in micelles, and in supramicellar assemblies (SA). Dodecanol can likewise exist free in solution, in micelles, and in SA. Concentrations of each are given, respectively, by

\[ C_{SDS} = C_f + C_m + C_a \]  
(92)

\[ C_D = C_{D,f} + C_{D,m} + C_{D,a} \]  
(93)

There are 4 principal SDS concentration regimes of interest, shown by the
dashed vertical bars in Figure 4.4.

\[ C_b \leq C_1 \]
\[ C_p \leq C_2 < C_b \]
\[ C_e \leq C_3 < C_p \]
\[ 0 < C_4 < C_e \]

Equations 92 and 93 for \( C_{SDS} \) and \( C_D \) apply in all regimes.

In \( C_1 \) regime dodecanol is solubilized by SDS in a metastable micellar structure; Long term observation shows that crystal formation in \( C_1 \) regime is influenced by \( R \), ionic strength and temperature, which will be discussed later. Free SDS exists at \( C_f \sim \text{CMC} \). The concentration of SA is zero or negligible. The loading of the micelles \( r \), is given by

\[
r = C_{D,m} = \frac{RC_{SDS} - C_{D,f}}{C_{SDS} - \text{CMC}_R}
\]

in \( C_1 \) regime

(94)

where data show free dodecanol concentration \( C_{D,f} \) is constant for regimes \( C_1-C_3 \) (see below). \( \text{CMC}_R \) means CMC may vary slightly with \( R \).

At the start of \( C_2 \) regime, \( C_b \), micelles are saturated by \( D \) and in \( C_2 \) there are micelles, saturated SA, and free SDS. Micelle saturation loading at \( C_b \) is \( r_{\text{max}} \).

\[
r_{\text{max}} = \frac{RC_b - C_{D,f}}{C_b - \text{CMC}_R}
\]

(95)

This implies linearity of \( 1/C_b \) vs. \( R \).
where it is assumed that $\text{CMC}_R - \text{CMC}_{R=0}$. Figure 4.5 shows that linearity of $1/C_b$ vs $R$ is found experimentally from Figure 4.2 data and that

$$r_{\text{max}} = 0.126 \text{ for dodecanol in SDS @ [NaCl]=0}$$

$$\text{CMC} = 0.00218$$

![Figure 4.4](image.png)  
**Figure 4.4** $1/C_b$ vs $R$ from data in figure 4.2 (and other data not shown therein)
As $C_2$ decreases micelles disappear and more SA appear. One supposition is

$$C_a = C_b - C_2, \text{ in } C_2 \text{ regime} \quad (97)$$

In this regime light scattering (LS) is dominated by SA. This assertion is supported by the fact that LS drops abruptly in moving from regime $C_2$ into $C_1$, where spherical micelles of $M_w=25,000$ dominate. Hence, to a good approximation

$$I_R(q=0) \cong KM_{w,a} C_a = KM_{w,a} (C_b - C_2) \quad (98)$$

The similarity of the slopes in regime $C_2$ in both Figures 4.2 and 4.3 suggest, quite remarkably, that $M_{w,a}$ is virtually constant in all cases. Slope $S_2$ yields $M_{w,a}$

$$S_2 = \frac{\partial I_R(q=0)}{\partial C_2} = -KM_{w,a} \quad (99)$$

$S_2$ is of the ‘$S_2$ line’ in Figure 4.4, extrapolated to $q=0$. Taken over data in figures 2 and 3 and other data not shown,

$$M_{w,a} = 1.95 \times 10^7 \text{ g/mol} \pm 9\% \quad (100)$$

independent of both R and IS. The latter is counter-intuitive as it might be surmised that the supramicellar assemblies at high IS might be more massive due to electrostatic shielding.

Under the supposition of Equation 97

$$I_{R,\text{max}} = KM_{w,a} (C_b - C_p) \quad (101)$$

At $C_p$ SA have their maximum concentration $C_{a,\text{max}}$ and it is assumed $C_m=0$;
\[ C_p = C_{f,p} + C_{a,\text{max}} = C_{f,p} + \left( C_b - C_p \right) \] (102)

Figure 4.2 shows a weak dependence of \( C_p \) on \( R \). A linear fit, whose intercept should be \( \text{CMC}_{R=0} \), yields,

\[ C_p (g/cm^3) = 0.0021 + 0.0046R = C_{\text{MC dopant-free}} + \alpha R \] (103)

where \( \text{CMC}_{R=0}=0.0021 \) agrees well with other determinations and \( \alpha=0.0046 \) may represent a slight shift in equilibrium not incorporated in this first-stage model. \( C_p \) hence does not occur at the dopant-free CMC, and \( C_{\text{MC dopant-free}}>C_{f,p,R>0} \) since \((C_b-C_p)>(C_p-C_{\text{MC dopant-free}})\); e.g. at \( R=0.090 \) \( C_{a,\text{max}}=0.0045(g/cm^3) \).

This model hypothesizes that SA only exist when they are at the saturation level \( r_{\text{max}} \) of dodecanol. Hence in the \( C_3 \) regime \( (C_m=0) \), not only will SA be diluted as \( C_3 \) decreases, but SA will also disappear as the amount of dodecanol needed to maintain saturation drops. Hence the loss of LS is steeper than the figure 3 ‘dilution line’. \( r \) is now

\[ r = \frac{RC_3-C_{D,f}}{C_a} \text{ in } C_3 \text{ regime} \] (104)

By the saturation hypothesis \( r=r_{\text{max}} \) in all SA, so that \( C_a \) is

\[ C_a = \frac{RC_3-C_{D,f}}{r_{\text{max}}} \text{ in } C_3 \text{ regime} \] (105)

and LS in \( C_3 \) regime, again dominated by a diminishing amount of SA is
\[ I_R(q = 0) = KM_{w,at} \left( \frac{RC_3 - C_{D.f}}{r_{\text{max}}} \right) \] (106)

The LS slope in C3 regime S3, is of the ‘S3 line’ in figure 3, given by

\[ S_3 = \frac{\partial I_R(q = 0)}{\partial C_3} = KM_{w,at} \frac{R}{r_{\text{max}}} \] (107)

This shows that, unlike S2, S3 depends on R and S3 < S2

\[ \frac{S_3}{S_2} = \frac{R}{r_{\text{max}}} \] (108)

\( r_{\text{max}} \) is determined from S3/S2 vs R and yields from figure 5

\[ r_{\text{max}} = 0.126 \text{ from } S_3 / S_2 \text{ @ [NaCl] = 0} \] (109)

This is remarkably close to the value found by a completely different method --use of Cb and Cp vs R-- which makes no reference to data for C_{SDS} < C_p.
The agreement of $r_{\text{max}}$ by both the LS slope method and Equation 95 lends internal consistency to this model, especially as concerns the SA saturation hypothesis.

$r_{\text{max}}=0.094$ and $r_{\text{max}}=0.104$ were found by the two methods from Figure 4.3 data. The small discrepancy with the $[\text{NaCl}]=0$ data is likely not significant.

*In the C₄ regime*, where there is little scattering above SBS, SDS and dodecanol are in free monomeric form in solution and $C=\text{C}_4$ and $C_{\text{D},1}=\text{RC}_4$. Supposing that at $C_e$ dodecanol is at its solubility limit $C_{\text{D},0}$ implies
\[ C_{D,0} = RC_e \] (110)

Figure 4.7 show the linearity of \(1/C_e\) vs \(R\), and yields \(C_{D,0} = 7.4 \times 10^{-6} \text{ g/cm}^3\).

As seen in Figure 4.4, \(C_e\) is both the point where the dodecanol solubility limit in aqueous solution is reached and the point where SA begin to form. As such \(C_e\) could also be termed the Critical Supramicellar Assembly Concentration (CSAC). CSAC plays a role similar to the notion of Critical Aggregation Concentration (CAC), for example, when SDS interacts with polymers to form aggregates[92][93].

Figure 4.6 Determination of dodecanol solubility limit from data in figure 4.2 (and other data not shown therein)
This model does not account for the ‘fine structure’ of the LS peak, such as curvature and inflection in the C₃ regime. It also implies small discontinuities in Cᵡ and Cₐ at Cₚ. More refined models will more closely address mass-balance, introduce thermodynamic considerations, and whether Cₘ=0 at Cₚ and rₘₐₓₘᵢｃｅｌｌₑₜ= rₘₐₓₜ,ＳＡ.

**Morphological conjectures based on Rₑ and Mₜ,a**

Kc/I vs q² yields <S²>ᵢ, which is independent of R and IS. <S²>ᵢ1/² = 83nm ± 20% was found for all Figure 4.2 and 4.3 data. It is counter-intuitive that <S²>ᵢ1/² is independent of IS. Preliminary notions of SA morphology can be conjectured. If the supramicellar assemblies were spheres

\[ R = \sqrt[3]{\frac{5}{3}} Rₘ = 107nm \]  

(111)

The mass, assuming ρ≈1g/cm³ is 3.1x10⁹g/mole, which, ignoring averaging effects from use of Mₜ and <S²>ᵢ is >150Mₜ,a. Hence, SA are non-spheroidal, perhaps branched, ‘star-like’, disk-like, or wormlike. Although there is no a priori reason to consider SA wormlike, a test can be made using structural assumptions[94][95][96]; wormlike surfactant micelle tube radius R≈1.5nm and ~20 surfactants/nm of length. With this SDS has 5,760(g/mole-nm), so that with
$M_w=1.13 \times 10^7 \text{g/mole}$, the contour length $L$, is 3,380nm. Using the coil limit of the wormlike chain model and the apparent persistence length $L_p$

$$<S^2> = \frac{LL_p'}{3}$$

(112)

yields $L_p' \sim 6.1 \text{nm}$, (ignoring excluded volume effects). While $L_p'$ is long compared to a flexible polymer this value is somewhat smaller than small angle neutron scattering (SANS) determinations of $L_p \sim 10-40 \text{nm}$.

Interestingly, whereas the myriad wormlike micellar systems are frequently found at much higher surfactant concentrations and are used for rheological control of fluids, the SA occur at low $C_{SDS}$ and had no readily measurable effect on the SDS solution viscosity in the LS peak region.

There is not sufficient evidence for wormlike or other particular morphology at this point. A thin disk, for example, would allow the dodecanol to be parallel to SDS and have its OH group exposed to the aqueous solution.

Inline filters of different sizes were used during the ACM experiments to make sure the particle size and LS peak were not artificially controlled due to the filtration. Figure 4.8 shows that the overlapping of the LS peaks for SDS solutions filtered by 0.45micron and 5micron and unfiltered solution. The character of the LS peak is not altered by these types of filtration.
DLS was also used to monitor the light scattering intensity of stock SDS solutions of different concentrations so as to eliminate the possible artifacts from mixing and flowing during the ACM gradient ramping. Figure 4.9 confirms that the light scattering intensity from batch mode has similar light scattering peak for doped SDS solution as in ACM experiments.
The discussion above is not limited to the interaction between SDS and dodecanol. Figure 4.10 shows that DTABr/Dodecanol mixture has similar light scattering peaks around the CMC of DTAB.

The complex LS peak structure is reproducible and Figure 4.10 shows examples at two values of R for DTABr/dodecanol in 10mM NaCl. Figure 4.11 shows $I_R(90^\circ)$ vs C$_{DTAB}$ at different IS and fixed R=0.066. All have complex peak structures, but the details of the peaks change with IS.

The sharp peaks may correspond to SA sub-structure rearrangements or
impurities besides dodecanol and constitutes an open question for further research. Understanding the origin of the ‘fine structure’ in the simpler SDS/dodecanol peaks may help in unraveling the origin of the multipeak structure in DTABr/dodecanol.

Figure 4.9  LS peaks for DTABr/dodecanol in 10mM NaCl
Same type of analysis carried out for SDS/dodecanol is applied to DTABr/dodecanol. The inset in Figures 4.10 shows the $I_{R,\text{max}}$ of DTAB LS peak has similar linear relation with respect to $R$, as for SDS. The $1/C_b$ vs $R$ plot gives $r_{\text{max}} = 0.18$, higher than for SDS/dodecanol.

Similar light scattering peaks are also found in SDS and DTAB solutions when dodecane is used as hydrophobic dopant. This indicates the discussion above is a fundamental phenomenon of surfactant system with hydrophobic impurity rather than the special case between SDS and Dodecanol.
Non-equilibrium aspects of doped micelles

As shown in Figure 4.11, doped SDS solutions are metastable. After standing for several days at room temperature, the doped SDS micelles solutions start to precipitate needle-like crystals. Neither dodecanol solutions alone or pure SDS solutions yielded crystals for several months. This is in fact a quite abnormal phenomenon given that the solubility of SDS in water at room temperature is about 10 times more than the concentration of the SDS solutions used and that the melting point of dodecanol is 24°C. To determine what the precipitate consists of, the
precipitated crystals were separated from the solution by centrifugation, and washed in an excess of cold water several times to obtain the final precipitate samples. A rough measurement of the precipitate’s melting point shows no visible change on the precipitate when the temperature increases from room temperature to 100°C. Further elemental analysis on the crystals from payload SDS micelles solution (C_{sds}=12.6\text{mg/ml}, R=0.09) by EDS shows the existence of 8% (weight percent) sulfur inside the precipitates, as shown in Figure 4.13. This indicates the existence of SDS in the released particles from micelles solution. i.e. an SDS/dodecanol interaction is required for crystallization.

![Figure 4.12 EDS analysis on precipitated crystals](image)
The dilution of SDS/dodecanol solutions into the LS peak regime produces the supramicellar assemblies, which are themselves metastable; such solutions also produce crystals over time. It is surmised that these crystals are the same as those formed in doped systems at $C_{SDS} \gg C_{MC}$.

Macroscopic observation shows that the precipitation rate depends on $R$, IS, temperature, and $C_{SDS}$. For example, for the solution with the same doping level and the same surfactant concentration, higher ionic strength will accelerate the precipitation. This actually agrees with the $A_2$ results from the static light scattering. Figure 4.14 shows the $A_2$ vs Ionic strength for SDS solution with and without dopant above CMC. As discussed before, $A_2$ characterizes the electrostatic excluded volume of micelles. The decrease of $A_2$ indicates the decrease of repulsive force, which leads to the aggregation between surfactant micelles. The much lower $A_2$ for doped SDS micelle solution in 200mM NaCl shows a much weaker repulsion between surfactant micelles, which may facilitate the precipitation of doped SDS micelle solutions. More results about the precipitation kinetics of Doped SDS solutions will be discussed in the SMSLS section.
An extended application of the ACM analysis on surfactant/hydrophobic dopant system is to evaluate the efficiency of dispersants. Surfactants have been widely used in the formulation of Oil dispersants since the existence of surfactants lowers the interfacial tension, thus reducing the energy required to mix the oil as discrete droplets into the water phase. A popular understanding is that the encapsulation of surfactant micelles to hydrophobic materials plays an important role in this process. However, the loading capacity of dodecanol in SDS is around 10% as shown in previous results, suggesting that the equilibrium loading of small micelles with hydrophobic materials is not efficient. To further explore the mechanism of the dispersing effect, the loading capacity of crude oil in Corexit 9500,
the oil dispersant used in BP oil spill case, is studied by Thermogravimetric analysis (TGA).

The TGA weight loss profiles (data not shown) for water, Oil, Corexit 9500 are obtained respectively first, indicating that the water is burned off between 100 and 150°C. The Oil is burned off between 180 and 240°C, and the Corexit 9500 is burned off between 100 and 520°C because of its complicated formulation.

A mixture of water, oil, and Corexit 9500 is agitated until being homogenous. The water, oil, and Corexit 9500 volume ratio is 90:10:1. The ionic strength of the mixture is 150mM. The phase separation takes place in the mixture after it is left standing for a few hours as shown in the inset in Figure 4.15. The separated two layers are both in their respective equilibrium state.
Figure 4.14 Low loading capacity of Corexit 9500 in equilibrium
(Bottom layer/equilibrium state)

The TGA weight loss profile of the top layer solution (data not shown) is almost the same as the oil alone. This means that most oil stays on the top of the mixture solution after the phase separation, and there is no Corexit 9500 or water in the top layer. Figure 4.15 shows the TGA weight loss profile of the bottom layer solution, which includes several steps. After 150°C, there is no water left in the sample. From 180°C to 240°C, the sample mass loss is from the Corexit 9500 and
Oil mixture. The mass loss after 240°C is from Corexit 9500 alone.

While the exact composition ratio of oil to Corexit 9500 is not obtained here since it is difficult to separate oil and Corexit 9500 in the temperature range between 180°C and 240°C, the TGA results still provide a good estimate about the composition of the bottom layer. The oil/Corexit 9500 ratio is less than 1/5, indicating that bigger amount of Corexit 9500 is needed to encapsulate the oil. This confirms that equilibrium loading of small micelles with hydrophobic materials is not efficient at dispersing oil. A dynamic, non-equilibrium, transient macro-emulsification process with energy input from the ocean and atmosphere is required for more efficient hydrophobic entrapment. Since these energy inputs are not controllable, new research on oil entrapment agents is conducted to efficiently trap large amounts in equilibrium.

4.1.4 Conclusion

Massive, metastable supramicellar assemblies (SA) due to surfactant/dopant interaction appear in the LS peak region. At C_b dopant-saturated micelles start to interconnect into SA, via dodecanol/surfactant interactions. Remarkably, M_w,a is independent of IS and R. The majority of SDS in SA may have its Na⁺ associated and the net SA structure may have weak but non-zero charge, since IS greatly affects...
metastability lifetime.

A self-consistent three component model is proposed to explain the main features of the LS peak and how it changes in response to dopant loading and solution ionic strength. The model does not capture, however, the ‘fine structure’ of the LS peak, nor explain the much more complex, multi-peak behavior found for CTABr/dodecanol.

Preliminary studies with dodecane show similar LS peak behavior with SDS. It is not yet known to what class(es) of hydrophobic dopants SA are found and for which the simple model may be applicable. The current work shows, at any rate, that the LS peak does not signal ‘release’ of the dodecanol by micelles, as is commonly thought, rather, the peak delineates the reorganization of the SDS due to dodecanol into supramicellar assemblies. This work coupling with the results from other different characterization methods also demonstrate that the efficiency of surfactants as oil remediation agents depends on the creation of dynamic, unstable oil/surfactant emulsions by energy input from the ocean and atmosphere. Since these energy inputs are not controllable, it would be preferable to have oil dispersant agents that are effective in equilibrium.

Most of the contents of this section were published as Reference [97] and [117].
4.2 Polymeric Suppression of Dopant Enhance Surfactant Supramicellar Assemblies

4.2.1 Introduction

Interactions between water-soluble polymers and surfactants have been investigated for decades[98][99][100][101][102][103]. Neutral polymer poly(vinylpyrollidone) (PVP) and anionic surfactant SDS show high levels of association[104][105][106][107]. At the critical aggregation concentration (CAC) surfactants begin to associate with polymer to form a ‘necklace’ structure on the polymer.

The effect of polymer molecular weight, temperature and ionic strength (IS) on polymer-surfactant association has been studied by NMR and surface tension[108][109][110][111]. Surface plasmon resonance spectroscopy was used to follow the kinetics of polymer surfactant interaction and surfactant binding[112]. Static light scattering combining with viscosity[113] was used to show that PVP becomes electrically charged when SDS binds to it and shows polyelectrolyte-like behavior.

Few reports have considered the effect of polymers on the interaction between surfactants and hydrophobic dopants[114][115][116]. Our recent work[117] shows
that certain hydrophobic dopants and surfactants in solution lead to formation of large metastable ‘supramicellar assemblies’ (SA) in a concentration regime from near the CMC down to the dopant’s solubility limit; i.e. the surfactant micelles do not merely release their hydrophobic payload the CMC, but remain associated with it. This property may help understanding of dispersants; e.g. those used in oil spills, where it is often thought that the surfactant will release the oil below the CMC and re-coalesce, diminishing the effectiveness of the dispersant. The SA shows that is not necessarily the case. Here, it was found that adding PVP to solutions containing SA can completely suppress the formation of SA from near the CMC down to the CAC. Many industrial and medical applications involve the use of self-assembly of surfactants, which makes the study of the polymeric effect on surfactant micelle and hydrophobic dopant systems a topic of potentially broad interest.[118][119][120][121][122].

4.2.2 Materials and Experimental conditions

SDS (Sigma Aldrich >99%) and Polyvinylpyrrolidone (PVP) (Sigma Aldrich>99%, M_w=650,000g/M) were solubilized in aqueous NaCl solutions of ionic strength either 1mM or 10mM. Dodecanol was added into PVP/SDS mixture solution above CMC and stirred several hours at T=25°C. Deionized and filtered
water (Purelab® Ultra Laboratory Water Purification System) was used through the experiments. All the solutions were filtered with 0.45mm Millex-GS Millipore membrane filter.

The loading ratio of dodecanol in SDS, R, is:

\[ R = \frac{\text{mass of dodecanol}}{\text{mass of SDS}} \]

In the previous work, it was found that the maximum loading of dodecanol in SDS occurred at R=0.126 for [NaCl]=0. In this work the major trends are shown for R=0.033. The trends remain the same at higher and lower R.

Automatic continuous mixing (ACM) monitored light scattering intensity, refractive index, and viscosity of SDS/PVP/Dopants solutions during the continuous gradient of specific solution components like SDS or PVP, as previously described. The flow rate of the system is 1 ml/min.

The ACM experiments here are divided into three categories in this project:

(i) Increasing the concentration of doped or ‘pure’ SDS into different fixed concentration PVP solution. This path allows to start with polymer only solution, which is then gradually charged by SDS monomers. The effect of polymer concentration on supramicellar assemblies can be monitored in this way. The CAC of SDS and PVP, and the saturation point of PVP to SDS can also be obtained. The effect of hydrophobic dopant on the behavior of PVP/SDS solution is studied by
comparing the PVP/SDS interaction with PVP/SDS/Dodecanol interaction.

(ii) Increasing SDS concentration with different doping level R into constant concentration PVP. This allows further exploration on the effect of hydrophobic dopant on polymer surfactant interaction.

(iii) Increasing the concentration of PVP while keeping the concentration of pure/doped SDS unchanged around CMC. This helps explore the effect of neutral polymer on the formation of supramicellar assemblies.

4.2.3 Results and Discussion

Interaction between PVP and ‘pure’ SDS

The main I_R features of SDS/PVP interaction (Figure 4.16) have been considered in detail previously. The concentration around 7×10⁻⁴ g/cm³ at which I_R begins to decrease for the three highest concentrations of PVP is the critical aggregation concentration (CAC), where SDS begins associating with PVP. The strong drop in I_R for the three highest PVP concentrations is due to electrical charging of neutral PVP chains as SDS associates, with subsequent increase of the electrostatic excluded volume contribution to the second virial coefficient A₂. A minimum I_R is reached, which corresponds to the maximum loading capacity of SDS onto PVP, and maximum A₂. C_{SDS} at saturation C_{sat}, increases as C_{PVP}
increases, as expected, and the saturation at 1mM NaCl from Figure 4.16 is
$g(\text{SDS})/g(\text{PVP})_{\text{saturation}} \approx 0.82$. This is close to the saturation found previously, 0.70.

Above $C_{\text{sat}}$, SDS goes free into solution, in monomeric and/or micellar phases, both of which increase the solution’s bulk ionic strength (IS). The increasing IS lowers the electrostatic contribution to $A_2$ and so $I_R$ begins to rise. Uncharged PVP turned anionic via associated SDS has been referred to as a ‘pseudo-polyelectrolyte’[123].

The change of viscosity corresponds to the change of PVP chain conformation with the increase of SDS concentration. The inset in Figure 4.16 shows that the viscosity increases rapidly after the first inflection point because of the increase of the electrostatic excluded volume. Then, the slope of the viscosity decreases after the second inflection point when PVP is saturated to SDS, and the slight increase of viscosity is due to the increased concentration of SDS. So, the first inflection point corresponds to the CAC of SDS and PVP, and the second point is the saturation point of PVP to SDS. They agree with the numbers from LS intensity.
Interaction between PVP and doped SDS

The addition of the small amount of dodecanol dramatically affects $I_R$, seen in Figure 4.17, which also shows the various concentration regimes and boundary concentrations, discussed below. Among the striking contrasts between Figures 4.16 and 4.17: i) Increasing $C_{PVP}$ drastically suppresses the large LSP obtained for $C_{PVP}=0$. ii) Scattering below CAC is a linear superposition of IR from PVP and SA. As a result, the initial slope at low $C_{SDS}$ is the same for all $C_{PVP}$, including...
$C_{PVP}=0$. iii) A well-defined ‘scattering crossover concentration’ occurs at $C_{SDS}=0.0026 \text{g/cm}^3$. $I_R$ is virtually independent of $C_{PVP}$ at the scattering crossover concentration, so that this concentration may also be termed an ‘iso-scattering point’.

Figure 4.16 $I_R$ vs $C_{SDS}$ for several $C_{PVP}$ at IS=1mM, $R=0.033$

Features i-iii can be explained in a way consistent with the interaction model of SDS/PVP.
(i) *Suppression of the large scattering peak as $C_{PVP}$ increases.*

LSP observed as systems of SDS/dodecanol are diluted towards the CMC are hypothesized to be due to the formation of supramolecular assemblies (SA), which begins during the dilution when $[\text{dodecanol}]/[\text{SDS}]$ in the micelles reaches its saturation value $r_{\text{max}}=0.12621$. These metastable, large structures, over two orders of magnitude more massive than normal surfactant micelles, are composed of surfactant and dodecanol; i.e. the pronounced LSP are not due to release of dodecanol from micelles as CMC is approached, but rather to large surfactant structures. The ‘anatomy’ of the LSP due to the formation of these structures has been given in detail in reference [117].

*The hypothesis for LSP suppression when PVP is added.* In the regime from the CAC up to $C_{\text{sat}}$, the binding energy of SDS to PVP is great enough that when dodecanol is added to PVP/SDS the dodecanol associates with the SDS bound to the PVP without dislodging the SDS from the PVP. This is seen by the decreasing magnitude of the LSP in Figure 4.17. When a relatively small amount of PVP is added, it binds as much SDS possible up to its $C_{\text{sat}}$, leaving the rest of the SDS in the form of SA, as seen in the diminished but still existent peaks in Figure 4.17 for PVP=0.2 and 0.5mg/ml. When sufficient PVP (1 and 2mg/ml in Figure 4.17) is added to bind all SDS in concentration regimes 2, 3, and 4, that is, for
CAC<C<sub>SDS</sub><C<sub>b</sub> the LSP disappears completely and the behavior closely resembles the PVP/SDS system without dodecanol, since no SA form to co-exist with the PVP/SDS in this regime. The initial minor LSP at high CPVP is explained by ii) and iii).

**ii) There is a ‘quasi-iso-scattering point’ near the CAC**

Data for C<sub>c</sub><C<sub>SDS</sub><CAC indicate dodecanol associates with SDS to form SA, as previously found, down to the solubility limit of dodecanol in water, C<sub>d</sub>=RC<sub>c</sub>=7.4x10<sup>-6</sup>g/cm<sup>3</sup>, the same value previously found. Hence, the scattering in this regime is the linear superposition of that due to the SA I<sub>R,SA</sub>, and that of the bare PVP I<sub>R,PVP</sub>. The existence of the SA is a clear demonstration of how free SDS exists for C<sub>SDS</sub><CAC and associates with dodecanol; Subtracting off I<sub>R,PVP</sub> from I<sub>R,total</sub> in Figure 4.17 yields overlapping data as shown in Figure 4.18.

The additivity of the I<sub>R</sub> data in this regime shows there is little interaction between the bare PVP and the SA. In Figure 4.17 I<sub>R</sub> converge in a narrow concentration band around C<sub>SDS</sub>=8.4x10<sup>-4</sup>g/cm<sup>3</sup>. 
Figure 4.17 Nearly overlapped LS for doped SDS/PVP mixture after subtracting polymer baseline in the concentration regime, $C_e < C_{SDS} < CAC$

Another means of verifying the linear superposition of the scattering is that the initial slope $\frac{\partial I_R}{\partial C_{SDS}}$ at low $C_{SDS}$ is the same for all $C_{PVP}$. This follows from linear superpositions, since $I_R$ in this regime is additive; i.e.

$$I_R = I_{R,PVP} + I_{R,SA}$$ (114)

$I_{R,PVP}$ is independent of $C_{SDS}$, since there is no association of SDS and PVP in this regime, and hence $\frac{\partial I_R}{\partial C_{SDS}}$ is independent of $C_{PVP}$ and depends only on the
association of dodecanol with SDS to form SA. The constant slope, \( \frac{\partial I_R}{\partial C_{SDS}} \), is clearly seen for the five data sets in Figure 4.17 over the regime \( Ce<C_{SDS}<CAC \).

iii) A scattering cross-over concentration occurs at \( C_{SDS}=0.0026 \text{ g/cm}^3 \)

This is the only point in the wide range \( Ce<C_{SDS}<Cb \) where \( I_R \) remains almost unchanged by any \( C_{PVP} \). Whereas \( I_R \) below CAC is described by linear superposition of \( I_R \) from PVP and SA, there is no a priori reason there should be a unique cross-over or ‘iso-scattering’ concentration--it is not merely a linear superposition of \( I_R \) of the scattering components--although there must necessarily be a cross-over of the LS intensity curves above \( C_b \), which can be readily understood as follows.

The \( I_R \) magnitudes in the LS peak regime decrease as \( C_{PVP} \) increases because the PVP/SDS associations decrease the SA population, and the PVP/SDS associations are over an order of magnitude less massive than the SA (approximately \( 7 \times 10^5 \text{ g/mole} \) vs \( 10^7 \text{ g/mole} \), respectively). Since \( I_R \) are hence inverted in order of \( C_{PVP} \) in this regime, they must cross each other to regain their expected order of \( I_R \) increasing with \( C_{PVP} \) for \( C_{SDS}>C_b \), when there are no longer any SA left and scattering is dominated by the PVP/SDS associations (and with \( C_{PVP} \) not high
enough for $A_3$ to significantly diminish $I_{R,PVP}$. This crossover is clearly seen to occur at the iso-scattering point in Figure 4.17. Again, there is no reason the cross-over should occur at a single SDS concentration.

To summarize this effect; the ‘inversion’ of the order of $I_R$ in the regime $CAC<C_{SDS}<C_{isoscattering}$ is understood in terms of the PVP/SDS association suppressing the formation of SA which are much more massive ($\sim 10^7$ g/M) than both the PVP associated with SDS ($\sim 10^6$ g/M) and SDS micelles ($\sim 10^4$ g/M). That they must cross and regain their order, increasing with increasing $C_{PVP}$ for $C_{SDS}>C_b$ is understood on the basis that SA do not exist above $C_b$ and that, since the PVP is so much more massive than SDS micelles, the PVP scattering must dominate. What is left unexplained is why the crossing occurs at a unique point, rather than being smeared out over the regime $C_{P,SDS}<C<C_b$. It may be that the relative narrowness of this regime, $C_{SDS} 0.0022 -0.0029$ g/cm$^3$ makes the existence of the iso-scattering point more fortuitous than fundamental. Figure 4.19 shows that an iso-scattering point also exists at 10mM NaCl, along with the other trends seen in Figure 4.17, albeit with a large shift in the features towards lower values of $C_{SDS}$, as expected and recently explored.
Figure 4.18  $I_R$ and viscosity vs $C_{SDS}$ for $R=0.033$ and various concentrations of PVP at IS=10mM

The iso-scattering point may appear similar to an isosbestic point; e.g when a net spectrum is the linear sum of spectra from two co-existing species an isosbestic point occurs at a wavelength of constant spectral value, as one species changes into the other in a reaction. The similarity is lost immediately, however, when it is considered that the spectra in Figure 4.17 cannot be built by a linear superposition of $I_R$ data in Figure 4.16 with the type of pronounced LSP at $C_{PVP}=0$ in Figure 4.17. It is a non-linear effect.
The development of a quantitative model for the light scattering signatures is complex, since it involves computation of scattering, simultaneously taking into account the effects of i) loading of SDS onto PVP and saturation, ii) the quantitative effects on electrostatically enhanced $A_2$ and $A_3$ as PVP is electrically charged by SDS, iii) the effects of ionic strength on $A_2$ and $A_3$ from excess SDS above $C_{sat}$, iv) and the distribution of SDS between SA and SDS/PVP associations. It is noted, for example, that the steep drop in $I_R$ vs $C_{SDS}$ for high concentration PVP in Figure 4.16 (1mg/ml and 2mg/ml) is due chiefly to the increasing values of $A_2$ and $A_3$, as, in the absence of the virial coefficient effects the intensity should increase vs $C_{SDS}$. That this is indeed the case can be seen in $I_R$ for the lowest concentration PVP (0.2 mg/ml in Figure 4.16), where the concentration is low enough that the virial coefficient effects are negligible compared to the increase in the SDS/PVP associations as $C_{SDS}$ increases. While such a complex model is beyond the scope of this work, the data shown can be used by those involved in modeling surfactant/polymer/dopant interactions. Qualitatively, Figure 4.17 shows the ‘anatomy’ of IR behavior for SDS/Dodecanol/PVP to be used in a subsequent model. The SDS concentration regimes to be considered are:

**C1 regime:** $C_b < C_1 = C_{SDS}$

**C2 regime:** $C_p < C_2 = C_{SDS} < C_b$
C3 regime:  $C_{\text{sat}} < C_3 = C_{SDS} \leq C_p$

C4 regime:  $C_{CAC} < C_4 = C_{SDS} \leq C_{\text{sat}}$

C5 regime:  $C_e < C_5 = C_{SDS} \leq C_{CAC}$

C6 regime:  $0 \leq C_6 = C_{SDS} \leq C_e$

where each of these concentrations is defined as follows:

$C_b = C_{SDS}$ where dodecanol begins to saturate free micelles’ ability to hold dodecanol. This depends on $C_{PVP}$ since PVP inhibits the formation of free micelles by binding SDS.

$C_p = C_{SDS}$ where the LSP occurs, when LSP is not suppressed by PVP.

$C_{\text{sat}} = C_{SDS}$ that saturates PVP. This depends on $C_{PVP}$. The dependence of $C_{\text{sat}}$ on $C_{PVP}$ is seen at the inflection points for viscosity on the inset to Figure 4.19.

The first inflection point at low concentration of SDS corresponds to the CAC, and the second one at high concentration of SDS corresponds to $C_{\text{sat}}$

CAC=Critical aggregation concentration of SDS, when association between PVP and SDS begins. CAC is independent of $C_{PVP}$ in Figure 4.17

$C_e = C_{SDS}$ at which $C_{dodecanol} = R C_e$ is the solubility limit of dodecanol and none is associated with SDS.
**Effect of dopants level on the interaction between polymer and surfactant**

Previous analysis indicates that the LS behavior before CMC is dominated by the amount of massive SA. When the concentration of PVP and SDS are constant, only the doping level can affect the amount of SA and the light scattering.

**Figure 4.20** demonstrates the effect of doping level on the LS behavior for PVP/doped SDS mixture. The concentration of PVP remains unchanged at 0.5mg/ml. At the lower doping level, the LS behavior is similar to the one in PVP/SDS without dopants, except for the small LS peak at CAC. The increasing amplitude of LS peak around CAC is due to the increasing amount of SA with ascending dopants level before the binding between PVP and SDS happens.

At the higher doping level, the LS intensity keeps going up after CAC, and forms a huge peak around CMC, indicating that 0.5mg/ml PVP is not sufficient to suppress the formation of SA with increased doping level. The LS intensity here mainly depends on the amount of SA, rather than the interaction between PVP and SDS. At the higher concentration of SDS (C_{SDS}>>C_{CMS}), all dodecanol molecules are loaded inside the SDS micelles. The LS intensity is dominated by the concentration of PVP, which explains why the LS intensity of different doping levels resembles each other at the high concentration of SDS micelles. The inset viscosity results show that the CAC and C_{psp} appear to be independent of the amount of
dodecanol.

Figure 4.19 $I_R$ & viscosity vs $C_{SDS}$ for various $R$ in 0.5mg/ml PVP/doped SDS

**Figure 4.21** shows that the LSP around CMC (~1.3mg/ml) in doped SDS solutions completely disappears when sufficient PVP (2mg/ml) is added to bind all SDS in the $CAC<C_{SDS}<C_b$ regime. The LS behavior at different doping levels closely resembles each other, since no SA forms to co-exist with the PVP/SDS in
this regime. The doping level, which determines the amount of SA before the aggregation between PVP and SDS, decides the intensity of minor light scattering around CAC.

Figure 4.20  $I_R$ vs $C_{\text{SDS}}$ for various R in 2mg/ml PVP/doped SDS levels in the presence of 2mg/ml PVP

Figure 4.22 further demonstrates that the polymeric suppression of dopant enhanced surfactant SA. 1.26mg/ml is around the CMC of SDS in 10mM NaCl.
For ‘pure’ SDS solution or just salt water, the LS intensity only depends on the amount of added PVP, which increases as the concentration of PVP goes up. For doped SDS system with SA, with the addition of PVP in doped SDS solution, SDS monomers bind PVP chains as much as possible because of the binding energy difference between PVP/SDS and Dodecanol/SDS. The amount of supramicellar assemblies and the related LS intensity decrease with the increase of PVP concentration. When sufficient PVP is added into doped SDS solution, no more SA exists because the aggregation between PVP and SDS breaks down the structure of all SA. Then, LS intensity is dominated by the concentration of PVP. This also explains why the LS intensity for these three systems (PVP alone, PVP/SDS, PVP/SDS/Dodecanol) converge at the high concentration PVP.
Suppression of supramicellar assemblies by polyethylene oxide (PEO), and by PVP for dodecyl triethyl ammonium bromide (DTAB)

Suppression of supramicellar assemblies for dodecanol/SDS was also found using PEO, seen in Figure 4.23. When PVP was added to the dodecanol/DTAB there was peak suppression, as seen in Figure 4.24.
Figure 4.22 $I_R$ vs $C_{SDS}$ for several $C_{PEO}$ at IS=10mM, $R=0.033$.

Figure 4.23 $I_R$ vs $C_{DTAB}$ for several $C_{PVP}$ at IS=10mM, $R=0.0066$. 
Polymeric effects on the non-equilibrium aspects of doped micelles

The previous report mentions that SDS micelles solution loaded with dodecanol is in a metastable state. It begins to precipitate needle-like crystals after standing a while. Here, the existence of PVP is found to accelerate the instability and precipitation in doped SDS solutions. The details will be discussed in the next section-applications of SMSLS.

4.2.4 Conclusion

The addition of PVP to SDS/dodecanol solutions causes SDS and its associated dodecanol to bind tightly to the PVP at the expense of the supramicellar assemblies. This leads to a loss of SA commensurate with the amount of PVP. The PVP will bind SDS until it is saturated, leaving any excess in the form of SA in the SA regime $C_e < C_{SDS} < C_b$. The competition between PVP/SDS/dodecanol aggregates and SA in this concentration range is seen vividly in the LS data. As PVP/SDS/dodecanol associations increase at the expense of the SA the $I_R$ plummets since the mass of the former is over an order of magnitude smaller than that of the SA. This leads to an inversion in $I_R$ in this regime, where $I_R$ decreases as $C_{PVP}$ increases. Above $C_b$ no SA exist any longer so that $I_R$ returns to being dominated by the PVP/SDS/dodecanol associations, and hence becomes re-ordered to increase with
increasing $C_{\text{PVP}}$. As a result of this there must be a crossover of $I_R$ vs $C_{\text{SDS}}$ curves somewhere between $C_p < C_{SDS} < C_b$, so as to regain this order. The cross-over occurs at a fairly well-defined concentration, the iso-scattering point, and it is not known if the existence of this point is fundamental or simply fortuitous because the C2 regime is not very broad.

Below the CAC, the SA re-occur and exist as if the PVP were absent. This is also remarkable, showing that the system passes from domination by the PVP/SDS interaction above CAC, which destroys SA, to domination by SA below CAC where the PVP/SDS interaction ceases to be important.

Most of the contents of this section were published as Reference [124] and [125].

4.3 Applications of simultaneous multiple sample light scattering (SMSLS) on exploring the fundamental properties of surfactants

4.3.1 Introduction

A surfactant is an amphiphilic compound which includes both hydrophobic and hydrophilic groups on its chain. This unique structure provides the means of applying surfactants in different application areas such as food, health and cosmetic
products, and pharmaceutical industries. A better understanding of the fundamental properties of surfactant is crucial for the greater application of this significant compound. The critical micellization concentration (CMC) of surfactants is directly related to the chemical formulations. The cloud points of neutral surfactants limit the range of their applications. The enhanced solubilization of hydrophobic compound by surfactants directly influences the efficiency of the detergent and the formulation of pharmaceuticals.

Different methods and techniques have been developed to characterize the fundamental properties of surfactants. For instance, surface tension measurements and conductivity measurements have been widely used to determine the CMC of surfactants. Turbidity is a commonly used technique to study the cloud point of neutral surfactants. While these techniques and methods can be enough efficient to determine specific property of surfactants, most of them are labor-intensive, and some of them have strict requirement on experimental environment.

Static light scattering has been widely used to characterize the properties of polymers such as $M_w$, $R_g$ and virial coefficients $A_2$ and $A_3$. It also can be used to follow the aggregation, phase separation, and degradation of materials since the light scattering intensity is very sensitive to large aggregates. A new light scattering based
device SMSLS is developed based on this feature. Instead of monitoring one sample per measurement, it can continuously collect data from multiple samples without any interruption for a long time to study their time dependent behavior. The latest improvement on the thermal control system of SMSLS expands its application to the temperature-dependent process of polymer solutions. It has been used to study the stability of polymer and/or colloid solution, protein aggregation kinetics and polymerization process and so forth.

In this work, SMSLS is used to provide new ways to determine the cloud point of neutral surfactants and its related factors, the CMC of surfactants at different temperatures, solubilization of hydrophobic compound by surfactants, the stability of doped surfactant micelle solutions and all other phase related phenomena. The application of SMSLS to phase transition related phenomena provides more consistent and high throughput results comparing with traditional labor-intensive techniques. Its involvement in determining the temperature-dependent behavior of CMC significantly shortens the experiment time and reduces the error from the long-term evolution of solution properties.

4.3.2 Materials

Surfactants sodium dodecyl sulfate (SDS) (>99%), Polyvinylpyrrolidone (PVP)
reagent Triton X-100 (laboratory grade) and Dodecanol (>98%) were used as received from Sigma-Aldrich. Sodium chloride (Sigma Aldrich, >99+) and calcium chloride (Fisher Chemical, >99+) were the salts used to adjust the ionic strength of solutions.

The loading ratio R is \( R = \frac{\text{mass of dodecanol}}{\text{mass of SDS}} \).

4.3.3 Results and Discussion

1. Cloud point of neutral surfactants

Cloud point is a characteristic feature of poloxyethylene-based non-ionic surfactant system. With the increase of temperature, the hydration of the hydrophilic group reduces the hydrophilicity of surfactants containing poloxyethylene chains (most non-ionic surfactants). The onset temperature of the phase separation is defined as the cloud point. Most nonionic surfactants are used below their cloud point.

In this work, SMSLS is used to measure the cloud point of a common non-ionic surfactant, Triton X-100, and study the ionic strength effect on its cloud point. To demonstrate the new application of this technique, Triton X-100 solutions are made at 10mg/ml in different solvents, including water, and different ionic strength NaCl
and CaCl$_2$ solutions. Then, these surfactant solutions are heated and monitored continuously from 30°C to 80°C in 100 minutes by SMSLS. Figure 4.25 shows the selected light scattering behavior for Triton x-100 in water, 10mM NaCl and 10mM CaCl$_2$ over the temperature range from 25°C to 70°C.

As seen in Figure 4.25, no significant change of the light scattering intensity of Triton X-100 in water is observed in the first half of the experiment, when the temperature is below 60°C. However, its light scattering intensity increases dramatically in very short time while the temperature keeps increasing. The strong increased light scattering intensity indicates the aggregation, and that the phase separation happens in the surfactant solution. The previously dissolved Triton X-100 is no longer completely soluble at this temperature. The critical temperature point corresponding to the start of the rapid increase of light scattering is the cloud point of Triton X-100 in water.

An interesting phenomenon shown in Figure 4.25 is that the Triton X-100 in salt solutions reach their cloud points earlier than Triton X-100 does in water. Higher ionic strength significantly decreases the cloud point of neutral surfactants. This agrees with the reports that the existence of salt is unfavorable for the formation of hydrogen bonds between water molecule and ether group of the non-ionic surfactants, thus reducing the hydrophilicity of Triton X-100.
Another phenomenon found in this figure is that the light scattering intensities of Triton X-100 in 10mM CaCl₂ and 10mM NaCl almost overlap each other. Similar phenomenon is also observed at 50mM salt solutions (Data not shown). This indicates that the cloud point of Triton X-100 is independent of the valance of the salt, and only depends on the ionic strength which agrees with the result from the Debye–Hückel equation and other experimental results [132][133][134].

Figure 4.24  LS90 of 10mg/ml Triton X-100 in different solvents with respect to the temperature
2. Solubilization of hydrophobic compounds in surfactant solutions (Solubilizing agents)

An important application of surfactants is that surfactants can aggregate and form micelles after CMC to solubilize hydrophobic compounds. As soon as micelles start to form, the hydrophobic nucleus becomes a favorable location for hydrophobic molecules to stay in. The polar segments of surfactants form a hydrophilic shell to remove the contact of hydrophobic nucleus to water. This property is directly related to the efficiency of detergent and the formulation of pharmaceuticals. SMSLS is used here to provide the quantitative information of the enhanced solubilization of surfactant micelles to hydrophobic molecules.

To evaluate the enhanced solubilization of surfactants to hydrophobic molecules, SDS is chosen here as solubilizing agents. Diisopropylamine has very good solubility in water at room temperature. However, its solubility decreases dramatically with the increase of temperature. In this experiment, different concentration SDS solutions were made in water with 1.28% (mole%) diisopropylamine, and monitored by SMSLS. The temperature of the mixture was ramped up slowly from 30°C to 70°C to continuously provide the hydrophobic compounds, diisopropylamine, to SDS micelle solutions.
Figure 4.26 (a) shows the light scattering behavior of 1.28% (mole%) diisopropylamine in water over the temperature range from 30°C to 55°C. There is a clear critical point around 37°C. After that, the light scattering signal notably increases and becomes noisier. Similar to what happens in non-ionic surfactants, high temperature breaks the hydrogen bond between water molecules and amine groups, leading to a poorer solvent quality as its temperature rises. Some of the previously completely soluble diisopropylamine starts to precipitate from the solution.

Figure 4.26 (b)(c)(d) show the light scattering behavior of 1.28% (mole%) diisopropylamine in different concentration SDS solutions over the temperature range from 30°C to 55°C. For diisopropylamine solution with 5mg/ml SDS (Csds>CMC), light scattering signal keeps stable until the temperature reaches to about 43°C, at which, light scattering suddenly increases notably and becomes very noisy. The dramatic change of light scattering signal here corresponds to the precipitation of diisopropylamine. The shift of the critical temperature point from 37°C to 43°C is caused by the fact that the SDS micelles solubilize the previous precipitated diisopropylamine after 37°C, until the saturation of SDS micelles to the precipitated diisopropylamine is reached at 43°C. As expected, higher concentration SDS (8mg/ml) further increases the critical temperature to 47°C in Figure 4.26 (C)
because of the higher amount of loading capacity. When the amount of the SDS micelles is excessive, such as 30mg/ml in Figure 4.26 (d), there is no light scattering spike or phase separation in the mixture solution. All previously precipitated/insoluble diisopropylamine are loaded inside the SDS micelles.

Since SMSLS is capable of monitoring eight different samples simultaneously, the phase separation points taken from critical temperatures of different concentration SDS solutions are summarized in table 5.

![Figure 4.25 Ir(90) of 1.28% (mole%) diisopropylamine in the presence of different concentration SDS with respect to the temperature](image-url)
Table 5. The phase transition points of 1.28% diisopropylamine (Mole fraction) in the presence of different concentration SDS

<table>
<thead>
<tr>
<th>C_{SDS} (mg/ml)</th>
<th>0</th>
<th>0.5</th>
<th>2</th>
<th>5</th>
<th>8</th>
<th>10</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase separation point (°C)</td>
<td>37</td>
<td>38</td>
<td>39.5</td>
<td>43</td>
<td>47</td>
<td>56.5</td>
<td>62.6</td>
<td>N/A</td>
</tr>
</tbody>
</table>

The temperature effect on the hydrophilicity of diisopropylamine is dominant in the discussion above, and the results provide the quantitative information of the enhanced solubilization of surfactants to hydrophobic compounds. In order to get more accurate quantitative information of the loading capacity of SDS micelles, other types of interaction between SDS and diisopropylamine, such as the effect of surfactant counterions on the hydration of amine groups, and the temperature effect on CMC, have to be considered.

The application of SMSLS can also be extended to determine the binary phase diagram based on the method above. For instance, different concentration diisopropylamine water solutions are monitored simultaneously over certain temperature range, and the phase diagram can be obtained by connecting the critical phase transition points at different concentrations. Figure 4.27 and 4.28 show the diisopropylamine-water phase diagram and phenol-water phase diagram. They all very well agree with the findings in the available literature. However, the
experiment here is much more consistent and less labor intensive comparing with traditional methods.

![Figure 4.26](image1.png)  
**Figure 4.26** Binary phase diagram for water-diisopropylamine system

![Figure 4.27](image2.png)  
**Figure 4.27** Binary phase diagram for water-phenol system

3. CMC of surfactants at different temperatures

It is well known that the CMC of surfactants depends on temperature. Much theoretical and experimental research has been done to study the temperature effect on the CMC[135][136][137]. For most ionic surfactants, their CMC decreases first below room temperature, and then increases as temperature increases. Different reports show that there is a general trend for non-ionic surfactants, according to which the CMC decreases with temperature. Chen and colleagues find that there is
also a similar minimum CMC at higher temperature for non-ionic surfactants.

Multiple techniques such as titration calorimetry, surface tension, ultrasound, and conductivity meter, have been used to study the temperature dependence behavior of the CMC. However, most of the techniques require intensive work on getting the CMC at different temperatures. In addition, the complicated environmental control and long-term evolution of solution properties may introduce extra error.

As discussed in the previous work, there is a light scattering peak around the CMC of the doped surfactants, and the concentration corresponding to the light scatter peak is very close to the CMC of surfactants. Besides, the CMC of surfactants are not found to be affected by the doping levels. Here, SMSLS technique provides an efficient way to quickly determine the CMC of SDS at different temperatures based on this unique light scattering behavior of surfactants. To demonstrate this new application, seven different concentration SDS solutions were made in 5mM NaCl and continuously/simultaneously monitored by SMSLS.

The dopant was dodecanol, and the doping level of SDS solution was R=0.033. The initial temperature was set at 80°C at the beginning, and then, the temperature continuously decreased from 80°C to 30°C in 100 minutes.

Figure 4.29 shows the light scattering behavior of selected concentration doped SDS solutions over the wide temperature range between 35°C and 80°C. There is a
light scattering maximum/peak at certain temperatures for all doped SDS solutions. At room temperature, the 2.1 mg/ml SDS in 5mM NaCl is higher than its CMC of the same condition. With the increase of temperature, the CMC of SDS in 5mM NaCl and its related light scattering peak shift to higher concentration.

As shown in Figure 4.29, the LS intensity for 1.995mg/ml increases first as the light scattering peak approaches 2.1mg/ml during this process, and decreases after the LS peak and when the CMC passes through 2.1mg/ml. The maximum LS intensity is recorded at about 73.6°C. This indicates that at 73.6°C, the LS peak is located at that specific concentration, 2.1mg/ml, and it is the CMC of SDS at 73.6°C. The same method can be applied to all other samples. Figure 4.30 and Table 6 shows the CMC of SDS in 5mM NaCl verse temperature.

Comparing with traditional CMC-determination methods including surface tension and conductivity measurement, this method is completely automatic. More importantly, it only takes two to three hours at most to get the quantitative relation between the CMC of surfactants and temperatures, which significantly shortens the time consumed, and reduces the error from the evolution of solution properties. In addition, SMSLS has advantages over the traditional methods with respect to the control of experimental conditions such as temperature. Since a number of surfactants have been reported to have a similar light scattering behavior, this
method can become a very efficient and universal way to determine the CMC of surfactants.

Figure 4.28  Ir(90) of different concentration doped SDS solutions with respect to the temperature

Figure 4.29  The CMC of SDS in 5mM NaCl at different temperatures
Table 6. The CMC of SDS in 5mM NaCl at different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>42.6</th>
<th>46</th>
<th>53.4</th>
<th>59.3</th>
<th>63.1</th>
<th>66.5</th>
<th>73.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMC of SDS (mg/ml)</td>
<td>1.47</td>
<td>1.575</td>
<td>1.68</td>
<td>1.785</td>
<td>1.89</td>
<td>1.995</td>
<td>2.1</td>
</tr>
</tbody>
</table>

4. Stability of doped micelle solutions

As discussed in the previous work the doped SDS micelle solution is metastable, and precipitates needle-like crystals over time. The relative motion between the precipitated crystals and the incident laser beam leads to the noisy light scattering signal. SMSLS is used here to study the stability of doped micelle solutions and the related factors by monitoring the noise level of light scattering.

*Ionic strength effect on the stability of doped micelle solutions*

In this experiment, doped SDS solutions (r=0.066, C=0.63mg/ml) were made in different ionic strength (100mM, 400mM, 600mM) NaCl solutions. High ionic strength was used here to speed up the precipitation process and shorten the experiment time. All these samples were monitored by SMSLS without interruption for 24 hours. The temperature was set at 28°C, which is higher than the melting point of dodecanol to eliminate the precipitation of dodecanol caused by freezing.
Figure 4.31 shows the LS behavior of doped SDS solution of different ionic strength. With the increase of the ionic strength, the light scattering signal becomes noisier at beginning. The abnormal noisy light scattering signal in the figure corresponds to the relative motion of the precipitated crystals. Here, doped micelle solutions at lower ionic strength is more stable because adding salt facilitates the precipitation process by screening the electrostatic repulsion between the complex structures of SDS/dodecanol molecules. The light scattering signal returns to normal and becomes stable when the new equilibrium is reached after the precipitation.

![Figure 4.30 Ionic strength effect on the stability of doped SDS micelle solutions](image)
**Temperature effect on the stability of doped SDS solution**

The same doped SDS (R=0.066, C=0.63mg/ml, [NaCl]=600mM) solution was monitored by SMSLS at different temperatures(28°C, 33°C). Figure 4.32 shows the temperature effect on the stability of doped SDS micelle solutions. As explained above, the noisy light scattering signal at 28°C correspond to the precipitates in solutions. However, for doped micelle solution at 33°C, the light scattering signal is very stable during the same period. This may due to the lower water solubility of the dodecanol at lower temperature, which facilitates the precipitation of doped surfactant micelles. Other concentration doped SDS solutions were studied in the similar way, which help to show that the influence of temperature on the stability of doped micelle solutions is consistent. Although the precipitation takes place regardless of the concentration of the SDS, the SDS micelle solutions around its CMC appear to precipitate more than they do at the higher surfactant concentration above CMC (data not shown). In addition, adding neutral polymer PVP into the doped SDS solutions decreases the stability of solutions as the association between polymer chains and doped surfactant micelles provides preferential nucleation sites with less free energy barriers. All the factors discussed above are consistent with the macroscopic observation doped surfactant solutions.
5. Sensitive detection of ‘micro-phase transitions’

Phase transition phenomenon is a gradual process which takes a while to complete. The micro-phase transitions are ongoing after the critical temperature, which is difficult to be clearly defined by watching the turbidity. One big advantage of the light scattering based technique is its sensitive detection of ‘micro-phase transition’. Figure 4.33 shows light scattering behavior for diisopropylamine (1.28% mole%) / SDS (8mg/ml) mixture around the phase transition point. After the critical
phase transition point, it clearly shows that there are light scattering spikes corresponding to the every single fluctuation of temperature. These spikes indicate the ongoing of micro-phase transitions, and might be related to the Le Chatelier's Principle.

Figure 4.32 The response of LS with respect to the temperature fluctuation around the phase transition point of SDS/diisopropylmine solution.

4.3.4 Conclusion

SMSLS has been proved to be a powerful and sensitive technique for different applications. The cloud point of non-ionic surfactant Triton X-100 is obtained by
SMSLS, and it is found to be independent of the valance type, and depends on the ionic strength only. In addition, SMSLS is used to provide the quantitative information about the solubilization capacity of SDS micelles to the ‘hydrophobic’ compound, diisopropylamine.

A new method combining the light scattering behavior of doped SDS solutions and SMSLS is developed to determine the CMC of SDS at different temperatures. Also, the factors associating with the metastability of doped SDS micelle solutions are studied by SMSLS while the results agree with the macroscopic observation.

The application of SMSLS to phase transition related phenomena provides more consistent and high throughput results comparing with traditional labor-intensive techniques. Its involvement in determining the temperature-dependent behavior of CMC significantly shortens the experiment time and reduces the error from the long-term evolution of solution properties.

4.4 Second generation ACOMP

4.4.1 Introduction

Polymers with increasingly sophisticated properties are being constantly developed. Some of these are classified as ‘stimuli responsive polymers’, and have
the ability to respond to stimuli such as heat, light and changing solution conditions, including pH, ionic strength, solvent polarity, and the presence of specific molecules or agents. The form of response can be a phase change, conformational transition, micellization, supra-molecular assembly, entrapment or release of a guest molecule, among others.

Since the ACOMP was first developed in 1998, it has become an important addition to the area of online monitoring polymerization. Extensive work has been done using the ACOMP to explore the reaction kinetics, and optimize the polymerization process of free radical copolymerization[138], controlled radical copolymerization, atom transfer radical polymerization [139], reversible addition fragmentation chain transfer (RAFT) polymerization [140], and other types polymerization [141].

While the ACOMP has been proven to be a unique and important method to do the online monitoring of polymerization, current set-up of the ACOMP can only monitor how polymer behaves under single condition. Further characterization work is needed to see how polymer evolves under different external stimuli.

The goal of this work is to develop the second generation ACOMP (SGA), which can monitor the onset and evolution of stimuli responsive behavior during synthesis. This is achieved by coupling a custom-built multi-stage detector train to
the highly dilute, continuous sample stream issuing from the automatic sample extraction and conditioning stage. Earlier work has been done to monitor the response of poly(NIPAM)-based copolymers to different temperatures during synthesis, and how the Lower Critical Solution Temperature (LCST) varies with copolymer composition drift during synthesis [142]. Here, further improvement has been made on SGA to monitor the response of a copolyelectrolyte at each instant of its synthesis to ionic strength varying from 0.1mM to 250mM.

4.4.2 Materials and Methods

The well-studied copolymerization of acrylamide (AM) and styrene sulfonate (VB) is chosen in this research to validate the capability of the SGA. Acrylamide is a hydrophilic neutral monomer with reactivity ratio $r_{am}=0.18$ in AM/VB copolymerization, and styrene sulfonate is an anionic monomer with reactivity ratio $r_{vb}=2.14$ in AM/VB copolymerization. The difference in the reactivity ratios leads to a significant composition drift in free-radical batch copolymerization, which in turn affects the properties of AM/VB copolyelectrolyte.

The polymerization reaction is carried out with 37.5mg/ml VB (Fluka) and 12.9mg/ml AM (Sigma Aldrich) in water at 65°C in a three-next reactor equipped with a condenser.
The initiator, 2,2'-Azobis(2-methylpropionamidine)dihydrochloride (V50) is used as received from Sigma Aldrich.

The figure below shows the simplified schematic of the SGA. A custom-built multi-stage detector train is coupled to the end of the first generation ACOMP system.

![Diagram of ACOMP system](image)

Figure 4.33  The simplified schematic of the second generation ACOMP

During the synthesis of AM/VB copolymer, a small stream of polymer sample from the reactor is continuously extracted, diluted, and conditioned in the mixing chambers. After that, the conditioned polymer sample is continuously delivered to
the detector trains of the first generation ACOMP which consists of a home-built single capillary viscometer, a Brookhaven Instruments Corp. multi-angle light scattering detector (BI-$M_w$A), a Shimadzu differential refractometer (RID-10A), and a Shimadzu photodiode array UV/visible spectrophotometer (SPM-20A). This set-up allows the determination of the $M_w$, $R_g$, intrinsic viscosity, the conversion of monomers, and other properties of polymer products in water.

The SGA embodiment after the first generation ACOMP includes seven stages in this experiment. Each stage contains a home-built viscometer and a home-built right angle light scattering detector, which measure the characteristics of the polymer in the stream under a specific solution condition. The solutions in the syringes on the infusion syringe pump determine the conditions of solution in each stage. The response of copolyelectrolyte to different ionic strengths is the focus of this work, so the syringes are filled with solutions of different concentrations (2mM, 20mM, 200mM, 1M, 2M, 5M) NaCl.

When the polymer solution passes through each stage in series, it mixes with the infused NaCl solution. The ratio of infusion rate to the flow rate in the SGA embodiments determines the ionic strength of the polymer solutions. The infusion rate here is 3ml/hour, and the flow rate coming out of the first generation ACOMP is 1ml/min. Therefore, the ionic strength in the seven stages are 0 (control group),
0.1mM, 1mM, 10mM, 50mM, 100mM and 250mM. The response of polymers under various ionic strengths is followed by the light scattering and viscometer during the synthesis. A 0.22um filter is attached in front of each syringe to increase the signal/noise ratio.

4.4.3 Results and Discussion

This section presents some early results from the second generation ACOMP. Figure 4.35 shows raw data for VB/AM copolymerization reaction in water. The baseline signal for water, VB, and VB/AM mixture is obtained before the start of the reaction. As shown in the figure, the reaction starts after the initiator is added around 9000 s, and the UV signal decreases with the progress of polymerization. The 256nm UV signal is dominated by VB absorption, and the 206nm UV signal is dominated by AM absorption. Therefore, the approximate consumption of monomers during the synthesis can be determined. One interesting feature in the UV 206 signal is that the consumption of AM happens in two steps. The consumption rate of AM changes dramatically around 16000 s, which represents the composition drift due to different reactivity ratios of two monomers.
Figure 4.34 Raw light scattering and viscosity data at 0.1, 10, 100mM

The light scattering and specific viscosity under different ionic strengths demonstrate the polyelectrolyte property of the VB/AM copolymer. Here, the SGA continuously monitors how the polymer behaves under seven different ionic strengths simultaneously. Results of polymers in 0.1mM, 10mM and 100mM NaCl are shown in Figure 4.35. The AM/VB copolymer shows big specific viscosity at low ionic strength, and the specific viscosity decreases with the increase of the ionic strength. This is a typical behavior of polyelectrolytes. When VB/AM copolymer is
dissolved in water or low ionic strength NaCl solutions, the polymer chains expand because of the electrostatic repulsion from the charged groups on VB part. As the polymer solutions mix with high ionic strength NaCl solutions in the late stages, the addition of NaCl shields the electrostatic repulsion, and the electrostatic excluded volume of the polymer chains decreases. Therefore, the specific viscosity decreases. The increase of the light scattering with the increasing ionic strength can be attributed to the $A_2$ effect. Higher ionic strength shields the polymer chain interaction. The decreased $A_2$ leads to the increase of light scattering at higher ionic strength.

Figure 4.36 shows the total conversion and instantaneous comonomer fractional composition during the synthesis. The continuous measurements on comonomer concentrations are used to compute the average instantaneous molar fraction of monomers in the copolymer chain at any moment based on equation 115 & 116:

$$F_{inst, AM} = \frac{d[AM]/dt}{d[AM]/dt + d[VB]/dt} \quad (115)$$

$$F_{inst, VB} = \frac{d[VB]/dt}{d[AM]/dt + d[VB]/dt} \quad (116)$$

Since the reactive ratio of VB (2.14) is much bigger than the reactive ratio of AM (0.18) in this copolymerization reaction [143], VB monomers incorporate into the polymer chains at a much faster rate than AM monomer in the first phase of the
reaction. Thus, the instantaneous AM fractional composition, $F_{\text{inst,AM}}$, shows a slow increase in the beginning of the reaction. However, it changes dramatically as VB becomes less available, and more and more AM is incorporated in the polymer chains. When VB is exhausted, the remaining AM continues to homopolymerize, producing a blend of copolyelectrolyte and PAM homopolymer. Higher fraction of AM in the second phase also slows down the reaction and total conversion rate, $f_{\text{total}}$.

![Graph showing total conversion and instantaneous comonomer fractional composition](image)

**Figure 4.35** Total conversion and instantaneous comonomer fractional composition
**Figure 4.3** shows the effect of varying copolyelectrolyte composition on the light scattering and Virial coefficients. As discussed in the previous part, the composition of copolymer chains progressively changes from richer in VB to richer in AM or containing only AM toward the end of the reaction. Such a change is also directly reflected in the response of the light scattering to the varying copolyelectrolyte composition. **Figure 4.3** shows the light scattering intensity versus total fractional molar conversion $f_{\text{total}}$ under different ionic strengths (0.1mM, 1mM, 10mM, 100mM). Because of the high concentration of copolyelectrolytes solution in SGA detectors, strong third Virial coefficient $A_3$ effect is observed which causes the light scattering to decrease with the increasing polyelectrolyte concentration at low ionic strengths (0.1mM, 1mM, 10mM). At 100mm NaCl solution, high ionic strength partially shields the chain interaction of polyelectrolytes, and the $A_3$ effect is salted out. However, the $A_2$ effect is still strong. The light scattering intensity slightly increases and reaches to a plateau with the increasing polyelectrolyte concentration. One interesting feature in this figure is the light scattering under all ionic strengths increases a bit in the second phase of the reaction. This is due to the formation of large acrylamide homopolymer after VB is exhausted.
Figure 4.36 The effect of varying copolyelectrolyte composition on the light scattering and Virial coefficients

4.4.4 Conclusion

This section discusses the latest progress of the ACOMP system, and the development of the second generation ACOMP. Unlike the traditional ACOMP which focuses on the behavior of polymers under one specific condition, the seven stages detector trains on the SGA provide the opportunity to study the response of polymers under different external stimuli. It opens the possibility for understanding and optimizing the development of novel stimuli-responsive polymers.
In this research, the response of AM/VB copolyelectrolyte to different ionic strengths is followed by the SGA simultaneously for the first time. It is also correlated with the composition drift of the copolymers at any time. The effect of ionic strengths on Virial coefficients $A_2$ and $A_3$ during the synthesis of this copolymer is also discussed.

The development of a new quantitative model is to be carried out by new comers of the SGA field to further analyze the polymer physics contained in the data.

Most of the contents of this section were presented as Reference[144].
5 Conclusion

Extensive analysis using multi-angle light scattering combined with multiple techniques is carried out to study the two and three-component interaction in a polymer/surfactant/hydrophobic dopant system.

This work shows that certain hydrophobic dopants in surfactant solutions cause the formation of massive “supramicellar assemblies” near the CMC, characterized by a pronounced light scattering peak. A light scattering based model is proposed to explain the mechanism behind this light scattering peak, obtain the $M_w$ and particle size of the supramicellar assemblies, and quantify the loading capacity of surfactant micelles to hydrophobic dopants and solubility limit of dopants in solutions. The $M_w$ of supramicellar assemblies is found to be independent of both ionic strength and the amount of dopants. This work coupling with the results from other different characterization methods also demonstrate that the efficiency of surfactants as oil remediation agents depends on the creation of dynamic, unstable oil/surfactant emulsions by energy input from the ocean and atmosphere. Since these energy inputs are not controllable, it would be preferable to have oil dispersant agents that are effective in equilibrium.

Following this, I discuss the interaction among polymer, surfactant, and
hydrophobic molecules from both hydrodynamic and electrostatic aspects. As expected, the association between surfactant and polymer turns the neutral polymer into pseudo-polyelectrolyte. Moreover, the existence of neutral polymer suppresses the formation of “supramicellar assemblies” between surfactant and hydrophobic molecules. The critical association concentration between PVP and SDS is determined by light scattering based model for this polymer, surfactant, hydrophobic dopant three-component system.

The applications of simultaneous multiple sample light scattering (SMSLS) on exploring the fundamental properties of surfactants are also discussed in this work. I have demonstrated that SMSLS can be used to efficiently study the phase transition related behaviors such as the cloud point of neutral surfactant, the binary phase diagram, and the solubilization capacity of surfactant micelles to hydrophobic molecules. In addition, I have demonstrated that the involvement of SMSLS in determining the temperature-dependent behavior of CMC significantly shortens the experiment time and reduces the error from the long-term evolution of solution properties.

Finally, the second generation ACOMP (SGA) system is developed. The very first data produced by SGA are shown in this work. The response of AM/VB copolyelectrolyte to different ionic strengths during the synthesis is followed by the
SGA simultaneously for the first time. It is also correlated with the composition drift of the copolymers at any time. The effect of ionic strengths on Virial coefficients $A_2$ and $A_3$ during the synthesis of this copolymer is also discussed. A long and complicated process of analyzing the polymer physics contained in the data lies ahead for other people now entering the SGA field.
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