BEHAVIOR OF SURFACTANT MIXTURE AT SOLID/LIQUID AND OIL/LIQUID INTERFACE IN CHEMICAL FLOODING SYSTEMS

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ABSTRACT

The aim of the project is to develop and evaluate efficient novel surfactant mixtures for enhanced oil recovery. Preliminary ultra-filtration tests suggest that two kinds of micelles may exist in binary surfactant mixtures at different concentrations. Due to the important role played in interfacial processes by micelles as determined by their structures, focus of the current work is on the delineation of the relationship between such aggregate structures and chemical compositions of the surfactants. A novel analytical centrifuge application is explored to generate information on structures of different surfactants aggregates. In this report, optical systems, typical output of the analytical ultracentrifuge results and four basic experiments are discussed. Initial sedimentation velocity investigations were conducted using nonyl phenol ethoxylated decyl ether (NP-10) to choose the best analytical protocol, calculate the partial specific volume and obtain information on sedimentation coefficient, aggregation mass of micelles. The partial specific volume was calculated to be 0.920. Four softwares: OptimaTM XL-A/XL-I data analysis software, DCDT+, Svedberg and SEDFIT, were compared for the analysis of sedimentation velocity experimental data. The sedimentation coefficient and aggregation number of NP-10 micelles obtained using the first three softwares at 25^0C are 209, 127, and 111, respectively. The last one is closest to the result from Light Scattering. The reason for the differences in numbers obtained using the three softwares is discussed. Based on these tests, Svedberg and SEDFIT analysis are chosen for further studies. This approach using the analytical ultracentrifugation offers an unprecedented opportunity now to obtain important information on mixed micelles and their role in interfacial processes.

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INTRODUCTION

There is considerable amount of oil trapped, together with water and gas, in reservoirs made up of porous and permeable rocks after the traditional oil production. Various chemical methods have been under development in order to recover additional oil. These methods have been in general inadequate due to the high costs of the processes as well as significant loss of chemicals by adsorption on reservoir minerals and precipitation. There is a need to develop innovative and cost-effective reagent schemes to increase recovery from domestic oil reservoirs.

The proposed research is to help develop improved extraction processes that can mobilize some of the oil left untapped using conventional techniques. It is our plan to design and evaluate efficient novel mixtures of surfactants for enhanced oil recovery, especially in multi-components systems containing oil, polymers, emulsifiers and/or inorganics that are invariably present in the system. The key criterion for the successful application of the techniques using candidate surfactants is minimal loss of surfactants by adsorption and precipitation.

It is well known that surfactants can interact to form aggregates in solution (micelles) and at interfaces (hemimicelles) and these phenomena can have drastic effects on oil recovery processes. However, there is very little information on such interactions in the case of mixtures and on changes in the aggregate structures due to perturbations in the system properties. Our recent work has shown that the aggregation behavior of some surfactant mixtures is quite unusual both in solutions and at the solid-liquid interfaces: more than one type of mixed micelles can form and possibly co-exist in mixed surfactant solutions. This finding has both theoretical and practical implications. It has potential for applications to minimize interfacial tension between oil and the flooding media to facilitate oil liberation and, at the same time, to reduce adsorption of surfactants on reservoir rocks.

There is almost no information in the literature on the relationship between the micro-structures or performance of mixed surfactant aggregates and the chemical structure of the components in the mixtures. Also, there are no models with predictive capability for the formation of mixed micelles, co-existing or otherwise. It is the goal of this research to investigate the formation of aggregates in mixed systems and the dynamics of such formation and the effects of that on processes relevant to oil recovery. Major emphasis will be to determine the relationship between surfactant mixture parameters (type, mixing ratio) and the aggregates properties (shape, composition and structure of mixed micelles and hemimicelles). Based on these results, a model which can predict the formation and changes in surfactant aggregates in their mixtures will be developed.

In our previous work, a model [1] was proposed to account for the non-ideal behavior of surfactant mixtures in terms of the packing parameter, i.e., change in the structures of mixed micelles with concentration. Preliminary ultra-filtration tests also suggest that two kinds of micelles may co-exist in binary surfactant mixtures. Now it is our plan to use analytical ultracentrifuge to test the model and elucidate the relationship between mixed micelle formation and the structure of surfactant components. During this first reporting period, mineral samples, surfactants and other chemicals to be used in this project have been procured and characterized, protocol for analytical centrifugation was established and initial analytical ultracentrifuge tests were conducted to identify the best analytical method, calculate the partial specific volume and collect information on single surfactant systems.

EXPERIMENTAL

Surfactants:

Several typical ionic and nonionic surfactants were selected for this study. Anionic sodium dodecyl sulfate (SDS) of greater than 99% purity purchased from Fluka chemicals and cationic dodecyl trimethyl ammonium bromide (DTAB) of greater than 99% purity purchased from TCI Chemicals, Japan were used as received. Nonionic ethoxylated surfactants covering a wide range of hydrophobic and hydrophilic chain lengths, including ethoxylated alcohols ($C_nH_{2n+1}(CH_2CH_2O)_mH$ or C_nEO_m) and nonyl phenols, were purchased from Nikko Chemicals. Non-ionic sugar-based surfactants, n-alkyl-$-D-glucosides and n-alkyl-$-D-maltosides from Calbiochem were also used as received. The structure of n-dodecyl-$-D-maltoside is shown in Figure 1. Homologues of nonionic surfactants enables study of the effects of surfactant structure such as chain length of the hydrophobic tail and size of hydrophilic headgroups on mixed aggregates formation.

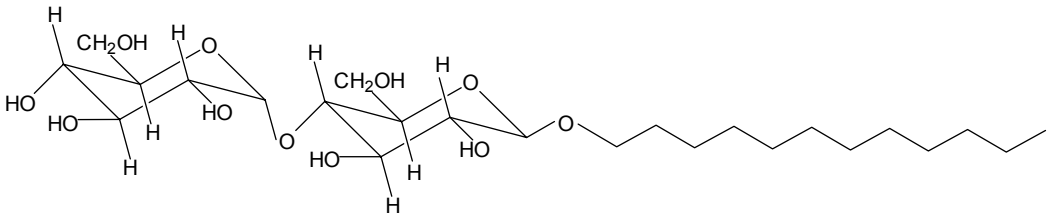


Figure 1. The Chemical Structures of Sugar-based Surfactant n-dodecyl-$-D-maltoside

All surfactants used for the study are listed in table 1

Table 1. Surfactants used and their formulas

Surfactant	formulas
Sodium dodecylsulfate	$C_{12}H_{23}SO_4Na$
Dodecyltrimethylammonium bromide	$[CH_3(CH_2)_{11}N(CH_3)_3]Br$
Polyethoxylated alcohol	$C_nH_{2n+1}(CH_2CH_2O)_mH$
Polyethoxylated nonyl phenol	$C_9H_{19}(C_6H_4)(CH_2CH_2O)_nH$
n-alkyl-$-D-glucopyranoside	$CH_3(CH_2)_n[C_6H_{10}O_5]OH$
n-alkyl-$-D-maltoside	$CH_3(CH_2)_n[C_6H_{10}O_5]_2OH$

Mineral Samples:

Alumina AKP-50 obtained from Sumitomo had a mean diameter of 0.2 ：m. The BET specific surface area measuring using nitrogen with a Quantasorb system was 10.8 m^2/g and the isoelectric point (iep) was 8.9. Silica obtained from Geltech was of a mean diameter of 0.1 ：m and the specific surface area of 12.21 m^2/g and the iep was around 2. These solids were chosen because of their low solubility and relative surface homogeneity with considerable amounts of information available in the literature.

Other Chemicals:

HCl and NaOH, used for pH adjusting, were A.C.S. grade certified (purity > 99.9%) and from Fisher Scientific Co.. Salts such as NaCl, KCl, $CaCl_2$, $AlCl_3$, all A.C.S. certified were used as received. Pyrene, a fluorescence probe, was obtained from Aldrich Chemicals and recrystallized from ethanol.

Water used in all the experiments was triple distilled, with a specific conductivity of less than 1.5：S^{-1} and was tested for the absence of organics using surface tension measurements.

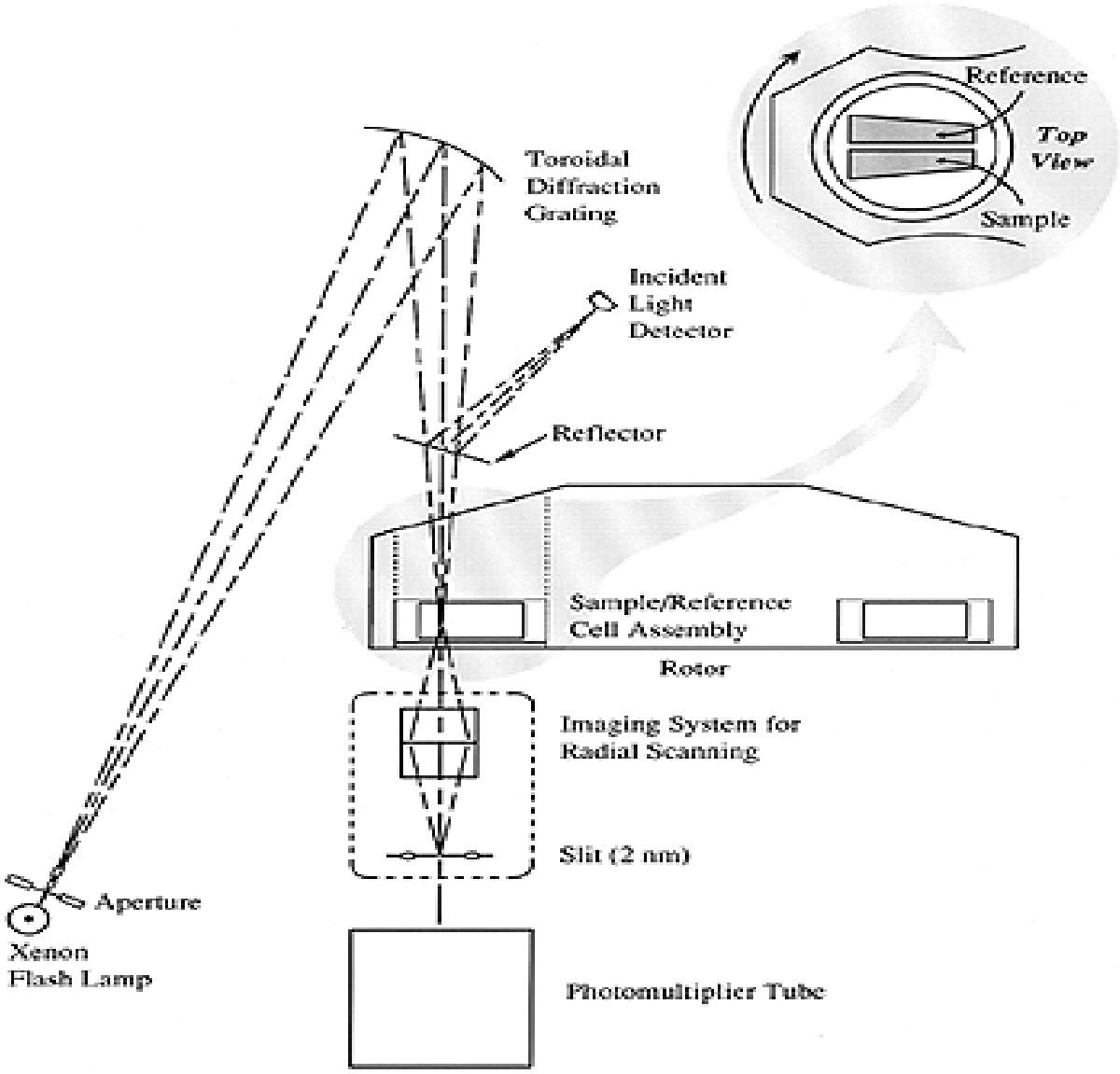
Analytical ultracentrifuge

The Optima XL-I analytical ultracentrifuge (Beckman Coutler)[2] with integrated optical system can measure solute concentration distributions in one or more sample solutions at high centrifugal forces. The data can yield many important thermodynamic and hydrodynamic properties of surfactant aggregates or macromolecules and their interactions. The system can analyze dilute as well as concentrated samples.

The XL-I optical system contains two detectors: UV absorbance and interference optical systems. Absorbance optical system uses a UV/Vis spectrophotometer to monitor concentration by absorption of light at wavelengths from 190-800 nm. The interference optical provides a cell image in which the total concentration is determined from the refractive index difference between the test sample and the reference sample at each radial position as indicated by the vertical displacement of a set of evenly spaced horizontal fringe. Figure 2 shows the optical systems of the analytical ultracentrifuge. [3] A xenon flashlamp serves as the light source. The lamp is fired as the sector of interest passes over the detector. A toroidally-curved diffraction grating selects single-wavelength light onto the sample. Since the intensity of light from the flash lamp varies somewhat from pulse to pulse, light from the diffraction grating is normalized by reflecting a small percentage onto a detector located at the virtual focal point of the monochromator system. Monochromatic light passes through the sample cell, which is bounded by two quartz windows. This cell contains both a sample sector and a solvent sector so that the intensity of light transmitted through the sample can be expressed with reference to the solvent, as measured by a photomultiplier tube positioned beneath the rotor. A lens-slit assembly moves as a unit to provide radial scans of these sectors.

The absorbance optical system is based on the fact that many macromolecular solutes absorb incident radiation at particular wavelengths. For solutes obeying Beer's law, the absorption is

linearly related to the molecular concentration. Thus, the radial distribution of the solute of interest, C(r), is readily determined from a radial scan of optical density.



Schematic diagram of the optical system of the Beckman Optima XL-A Analytical Ultracentrifuge From "Analytical Ultracentrifugation, Vol. I", Beckman Instruments, Inc.

Figure 2: Optical system of the Beckman Optima XL-A AUC.

The experiment begins with the sample mixed uniformly throughout the cell, so that a plot of concentration vs radius is a horizontal line (C(r) = constant). As sedimentation proceeds, molecules are depleted from the top of the solution column. This results in the formation of a trailing boundary for the concentration distribution.

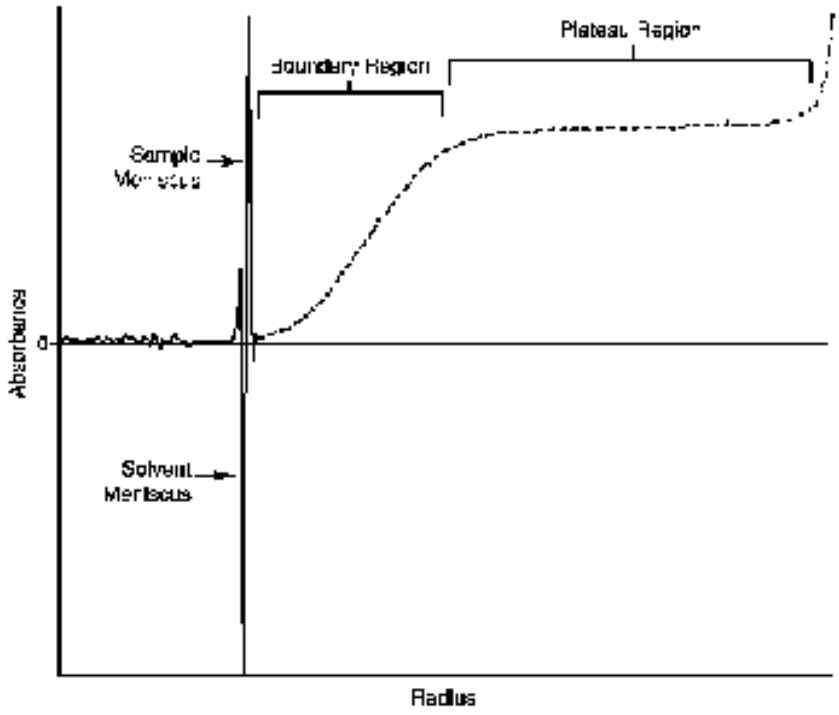


Figure 3: Typical boundary sedimentation data.

Figure 3 represents the absorbance of a solute in the sample sector compared to the reference sector. Sharp peaks result from the refraction of light away from the photomultiplier by the menisci in each sector. The remainder of the data consists of the boundary region in which the solute concentration increases rapidly to a reasonably constant value in the plateau region. Most of the information in a sedimentation velocity experiment is taken from analysis of the boundary. For example, the boundary will be sharp for a simple sedimentation involving one component. The sedimentation coefficient can be derived from the motion of the boundary midpoint. As an

alternative representation, the data may be presented as the derivative of the concentration function, or dC/dr. In this representation, each boundary segment appears as a discrete peak. The sedimentation coefficient is obtained from the radial motion of these peaks. The relative concentration of each sample component is determined from the area under each peak.

One feature of the plateau region is worth noting. Particles of greater radii will move faster than the smaller ones, thus pulling away from the latter. In addition, as the experiment progresses, particles beginning near the outermost portion of the solution column will be pulled against the outer wall of the sample cell, and will be replaced by particles from nearer the center of rotation. These latter particles enter a progressively increasing volume as they migrate outward through the sector-shaped cavity, and thus become more dilute.

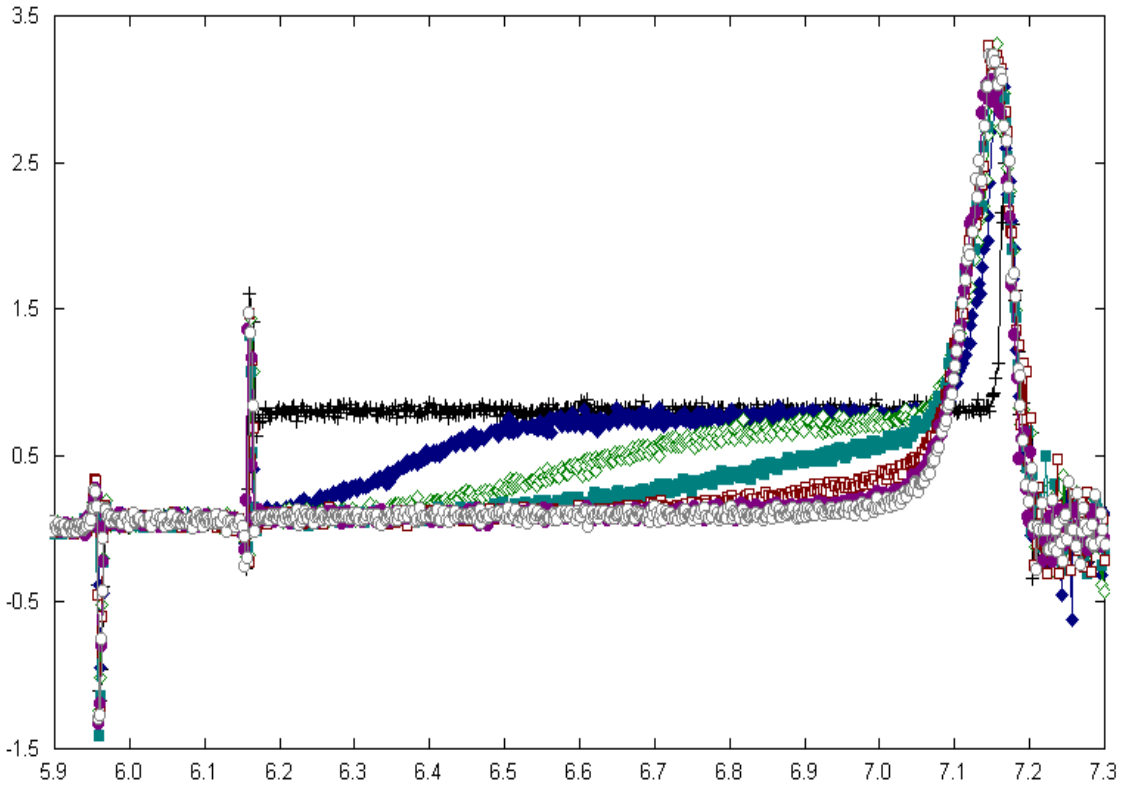


Figure 4 presents shifting boundaries at different rotation time. As sedimentation starts, the solute is distributed evenly along the radius. Boundary shifts gradually to the bottom of the cell with time

RESULTS AND DISCUSSION

Experimental Schemes

Basically, analytical ultracentrifuge(AUC) has four experimental schemes [4]:

1) sedimentation velocity experiment,

2) sedimentation equilibrium run,

3) density gradient run,

4) synthetic boundary experiment.

Sedimentation velocity experiment and sedimentation equilibrium run are the commonly used methods.

1. Generally, sedimentation velocity experiment is carried out at high centrifugal fields. When separation of mixture takes place, one can detect a step-like concentration profile. Each step corresponds to one species. Also, the sedimentation of molecules can be monitored. From the sedimentation velocity experiment, one can obtain information such as the rate of movement of a solute in a centrifugal field, an apparent weight average sedimentation coefficient, an apparent sedimentation coefficient diffusion function g(s*) from the time derivative of the concentration profile, a weight average diffusion coefficient and an estimated molecular weight (M). From the velocity of the sedimenting boundary, one can determine the sedimentation coefficient *s* according to:

$$s = \frac{ln(r / r_m)}{\omega^2 t}$$

where *r* is the position of the moving boundary, r_m the radial distance of the meniscus, *t* the time and ω the angular velocity. The sedimentation coefficient is a concentration and pressure dependent quantity which can be obtained by appropriate correction or the extrapolation to zero concentration.

A plot of ln(r/rm) vs. $\omega^2 t$ is a line with the slope equal to the sedimentation coefficient. The sedimentation coefficient is measured in the Svedberg (S) unit where $1S=10^{-13}$ s.

The molar mass of the sample can be calculated according to the Svedberg equation:

$$M = \frac{sRT}{D(1-\bar{v}\rho)}$$

where D is the diffusion coefficient, M the molar mass of the sample, $\bar{v}$ the partial specific volume, ρ the solvent density, R the gas constant and T the absolute temperature.

2. Sedimentation equilibrium experiment is performed either at moderate or at high centrifugal fields. The concentration gradient contains information about the molar mass of the sample, the second osmotic virial coefficient or interaction constants in the case of interacting systems. The advantage is that the detection of the concentration gradient is possible without disturbing the chemical equilibrium even for weak interactions. Sedimentation equilibrium analysis allows one to determine the following properties: macromolecular structure (molecular weight, or weight-average molecular weight if there is heterogeneity), association properties of macromolecules in solutions (stoichiometry, reversibility and association constant), heterogeneity (dissimilar non-self-associating components present) and nonideality (non-associative interactions between molecules due to shape or charge).

$$c(r) = c(a)\exp[M(1-\bar{v}\rho)\omega^2(r^2 - a^2)/2RT]$$

where $c(r)$ is the concentration at radial position r, $c(a)$ the concentration at the meniscus, a the radial distance of the meniscus, R gas constant and T absolute temperature.

3) Density gradient experiment is based on possible separation due to chemical structure in a

density gradient medium. Either high density salts or substances like sucrose are dissolved in water or a mixture of two organic solvents with very different densities is used. The sample will sediment/float to a position where its density matches that of the gradient. In the case of mixtures, this leads to a banding of the components due to their chemical structure/density.

4) Synthetic boundary experiment relies on the changes of a boundary between solution and solvent with time at low centrifugal fields where no sedimentation of the sample occurs. Such experiments require special cells where the solvent is layered upon the solution column under the action of a certain centrifugal field. Diffusion coefficient distribution could be derived in a single synthetic boundary experiment.

Calculating the Partial Specific Volume

Svedberg equation is the basis of analytical ultracentrifuge technique. Thus partial specific volume is a very important parameter. There are two ways to obtain the partial specific volume: theoretical calculation and by densiometer. Calculation method is fast and accurate for single component systems and systems with inorganic salts. Experimental method is especially useful for mixed systems.

So far, calculation method is chosen because only hydrodynamic properties of single surfactant are measured. Helmut Durchschlag and Peter Zipper's approach [5, 6] is adopted to calculate the partial volumes of surfactants and their mixtures in aqueous solutions. The method is based on Traube's additivity principle and concept of volume increments for atoms. This calculation procedure is developed for some special increments/decrements for co-volume, ring formation, ionization and linking tabulated volumes of inorganic ions.

Partial molar volumes, $\overline{V_c}$ is defined as:

$$\overline{V_c} = \sum V_i + V_{CV} + \sum V_{RF} - \sum V_{ES}$$

where *Vi* is the volume increment for any atom or atomic group, V_{CV} the correction due to the covolume, V_{RF} and V_{ES} take into account the decrease in volume caused by ring formation and ionization (electrostriction), respectively.

The partial specific volume, $\bar{v}_i$ of the ith component of a solution is defined as the change in total volume, ∂V , per unit mass upon adding an infinitesimal amount, ∂g_i , of component i at constant temperature, *T*, and pressure, *P*, and masses in grams, g_j, of all other components *j*:

$$\bar{v}_i = (\partial V / \partial g_i)_{T,P,g_j} \qquad \text{(j...i)}$$

The partial specific volume, is defined in an analogous way by substituting the number of grams, *g*, by the number of moles, *n*:

$$\bar{V}_i = (\partial V / \partial n_i)_{T,P,n_j} \qquad \text{(j...i)}$$

Usually, partial specific volumes, $\bar{v}$, are given in cm^3/g, and partial molar volumes, $\bar{V}$, in cm^3/mol. These two are related by:

$$\bar{v}_i = \bar{V} / M_i$$

where M_i is the molar mass of the ith component, in g/mol.

Reported experimental partial specific volumes of surfactants generally vary between 0.7 and 1.2 cm_3/g, depending on the nature of surfactants and the micellar state. The effect of micellization on the partial specific volume is also taken into account by introducing an additional volume increment V_{mic}. V_{mic} is influenced by various parameters (e.g., chain length and surface charge, shape and structure of micelles, aggregation number, CMC values, interaction between surfactants, solvent and cosolvents). The volumes of surfactants above CMC generally exceed the value below CMC by 0-6%. However, for most nonionic surfactants, no correction for micellization is necessary. Partial specific volume of nonyl phenol ethoxylated decyl ether (NP-10) is calculated according to the above method.

Table 2: Calculation of the partial specific volume of NP-10 Surfactant at 25°C

Name	V_C (cm3/mol)	M (g/mol)	$<_C$ (cm3 /g)
NP-10	606.5	658.9	0.920

Compared to values in literature [7], experimentally determined value for partial specific volume of Triton N-101 (a mixture between NP-9 and NP-10) is 0.922. The calculated result is very close to the experimental result.

It should be noted that the partial volumes are only valid for aqueous solutions at 25°C. Application of volumes at different temperatures requires the use of a temperature correction. For substances in aqueous solutions, temperature coefficient of 2-10 $\times 10^{-4}$ $cm^3g^{-1}K^{-1}$ has been reported in the literature, therefore, a value of 5 $\times 10^{-4}$ $cm^3g^{-1}K^{-1}$ for temperature correction may be used.

Data Analysis Softwares

Lamm equation is the basic equation for sedimentation velocity data analysis softwares. It describes the evolution of concentration distribution C(r, t) of a species with sedimentation coefficient s and diffusion coefficient D in a sector-shaped volume and in centrifuge field T^2t. It is a partial differential equation:

$$\frac{dc}{dt} = \frac{1}{r}\frac{d}{dr}[rD\frac{dc}{dr} - sw^2r^2c]$$

1. OptimaTM XL-A/XL-I data analysis software [2]

A customized OptimaTM XL-A/XL-I data analysis software is used for velocity and equilibrium experiments. The experimental analysis of sedimentation velocity experiments provides four models such as transport, second moment, sedimentation time derivative and flotation time

derivative. The transport method measures the total amount of solute transported across a boundary chosen in the plateau region of the data set. An advantage of the transport method is that it can be used to calculate a *s* value from early files in an experiment, because it does not require that the meniscus to be depleted of the solute. However, a more accurate analysis of the interference data can be obtained using the second moment method. The second moment method must use data with a flat lower plateau, indicating that the solute has moved away from, or become depleted at, the meniscus region of the cell.

Sedimentation time derivative analysis is used to calculate apparent sedimentation coefficient distribution functions, *g(s*)*, from the time derivative of the concentration profile of all particles in a system. In systems where particles are less dense than the solution they are suspended in, they float up from the bottom of the cell, and the flotation time derivative analysis is used to determine the density distribution for the system. Molecular weight could not be determined by this analysis because sedimentation does not occur.

Sedimentation time derivative method is the most commonly used method in sedimentation velocity experimental data analysis The molar mass, diffusion coefficient and sedimentation coefficient of 6×10^{-4}M NP-10 micelles are analyzed by time derivative method. Experimental conditions are below:

* Rotor speed: 40K rpm

* Scan No. used in the analysis: 20

* Detector: UV 273 nm and RI

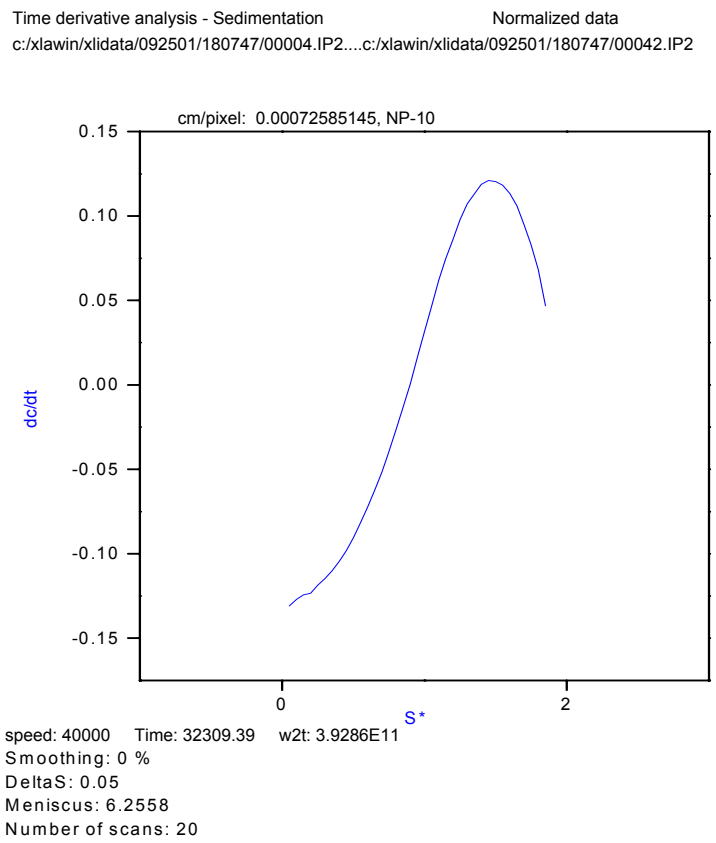
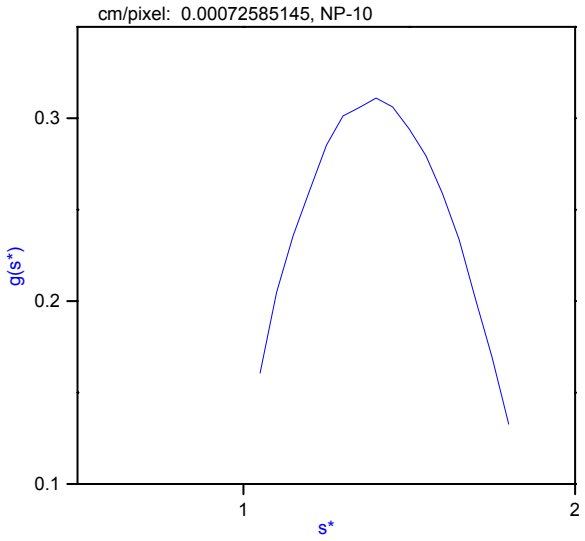


Figure 5. dc/dt vs. s* plot.

Figure 5 shows results obtained for sedimentation time derivative method. Here, s* denotes apparent sedimentation coefficient. Because the software does not eliminate the diffusion effect, this sedimentation coefficient is not the real sedimentation coefficient. A Gaussian's distribution could be applied for the apparent sedimentation coefficient as shown in figure 6.

Figure 7 shows the overlay of two curves. Results for the *g(s*)* are shown here: S*=1.40S, M=138KDa, D*=9.39e-8. From this aggregation mass, the aggregation No. is expected to be 209.

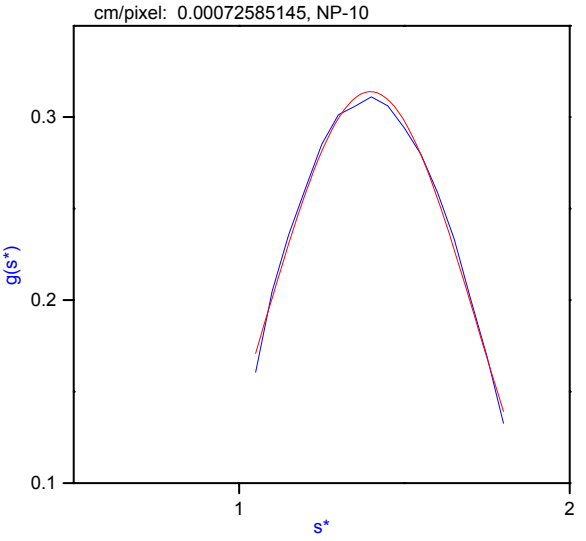
Time derivative analysis - Sedimentation Normalized data
c:/xlawin/xlidata/092501/180747/00004.IP2....c:/xlawin/xlidata/092501/180747/00042.I



speed: 40000 Time: 32309.39 w2t: 3.9286E11
Smoothing: 0 %
DeltaS: 0.05
Meniscus: 6.2558
Number of scans: 20

Figure 6. Gaussian's fit curve of apparent sedimentation coefficient.

Time derivative analysis - Sedimentation Normalized data
c:/xlawin/xlidata/092501/180747/00004.IP2....c:/xlawin/xlidata/092501/180747/00042.IP2



Peak	Sigma	D*	M	S*	Area
1	3.15377E-14	9.29698E-8	137952	1.39768E-13	0.24819

Speed : 40000
Time : 32309.39
W2t : 3.9286E11
Smoothing: 0 %
DeltaS : 0.05
Meniscus : 6.2558
Number of scans: 20
V-bar: 0.73
Rho : 1

Figure 7. Comparison of Gaussian's distribution results with experimental results.

Disadvantages:

a. It is very difficult to obtain g(s*) results for surfactant systems by this software. Gaussian distribution is the default analysis method. One of the virtue of Gaussian distribution is that the time difference dc/dt eliminates the time invariant noise usually encountered in interference optical data. However, the resolution of Gaussian distribution is poor.

b. This software sets partial specific volume and solvent density as default values. The partial specific volume is the same as that of proteins - 0.73 cm3/g and the solvent density is the same as that of water. The partial specific volume of the surfactant is quite different from that of protein.

c. Back diffusion effect is very severe in surfactant systems due to the small micellar size. The sedimentation coefficient distribution g (s*) using time derivative method does not eliminate the back diffusion effect. A small portion among the whole scans (usually less than 40 scans) has to be chosen to do analysis to keep the diffusion coefficient constant. Thus, the apparent sedimentation coefficient and molecular mass results do not reflect the real values.

2. DCDT+ software

DCDT+, developed by John Philo [8], directly fit the dc/dt curves [rather than g(s*)] to obtain the s and D (or M) values. This gives significantly more accurate results [~1% error in M instead of errors up to 10% through fitting g(s*)]. Fitting to dc/dt also provides an improved ability to resolve multiple species, and avoids some of the problems that g(s*) has with low molecular weight species. The function used to fit the dc/dt curves is the analytical time derivative of the modified Fujita-MacCosham function which is the approximate analytical solutions of Lamm equation. This software allows input of partial specif volume and solution density. The maximum scan No. is 99.

Modified Fujita-MacCosham function is described as below: This function gives the concentration c at any time t and radial position r in terms of dimensionless parameters

$$\tau \equiv 2s\omega^2 t \qquad x \equiv (V/V_0)^2 \qquad \varepsilon \equiv 2D/s\omega^2 r_0^2 \qquad Z = ln(x)$$

and z = ln(x), from the formula:

$$C = \frac{C_0 e^{-\tau}}{2}\left\{\begin{array}{c} 1 - erf\left[\dfrac{\tau - z}{2\sqrt{\varepsilon\tau}}(1+\alpha\tau)\right] \\ -\dfrac{2}{\sqrt{\pi}}\left(\dfrac{\tau}{\varepsilon}\right)^{1/2}\exp\left(\dfrac{-(\tau - z)^2}{4\varepsilon\tau}(1+\beta\varepsilon\tau)\right) \\ +\left(1+\dfrac{\tau + z}{\varepsilon}\right)\left(1 - erf\left[\dfrac{\tau + z}{2\sqrt{\varepsilon\tau}}\right]\right)\exp\left(\dfrac{z}{\varepsilon}\right) \end{array}\right\}$$

where C_0 is the loading concentration, r_0 is the meniscus position, and erf() is the error function. A and b are dimensionless numerical factors whose values were found empirically to be a = 0.2487 and b = 2.

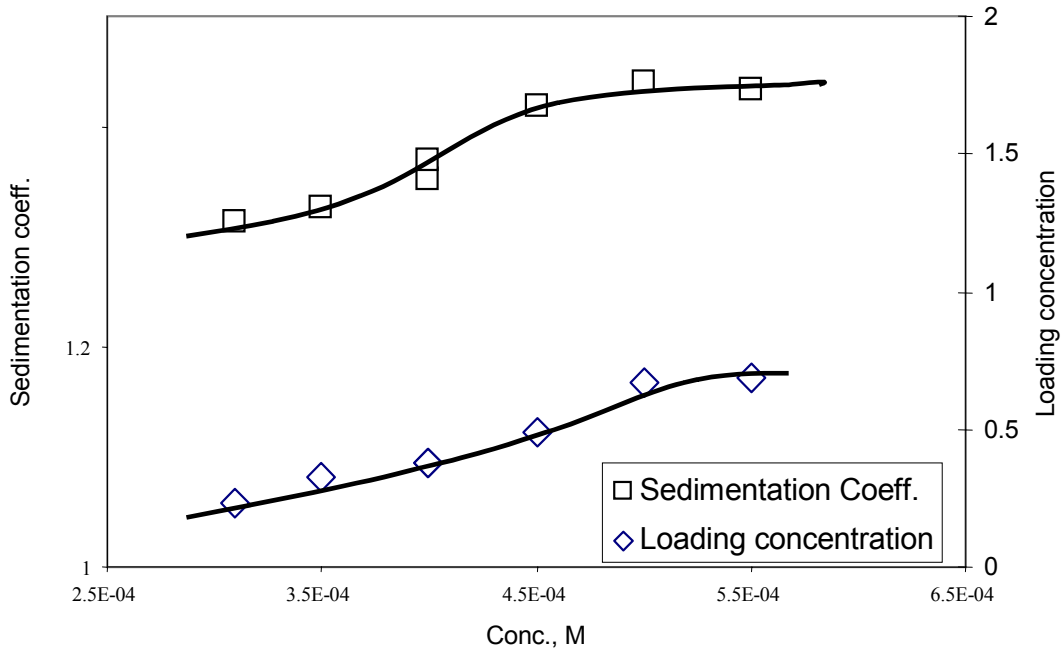


Figure 8. Effect of concentration on the loading concentration and sedimentation coefficient

Figure 8 shows that both loading concentration and sedimentation coefficient are linear with concentration. These trends agree with the theoretical prediction. By inputting the partial specific volume of NP-10, the aggregation masses are less than that from OptimaTM XL-A/XL-I data analysis software. The results are closer to the result observed by other technique such as light scattering [9]. Light scattering shows that the aggregation No. of NP-10 is around 100.

3. Svedberg software

SVEDBERG is particularly good for quantitative results and for resolving small amounts of minor species (e.g. 5-10% of a dimer). Its superior resolution over the DCDT method arises from the fact that it can fit data over a broad time range. Compared to g(s*) analysis with DCDT, SVEDBERG provides superior accuracy for s values, especially for small proteins (5-50 kDa), and significantly more accurate results for D or M of larger proteins (>100 kDa) [<~1% error instead of errors up to ~10% through fitting g(s*)].

For multi-species fits SVEDBERG also allows the user to constrain the properties of the species with respect to one another, forcing the constrained species to have hydrodynamic properties which are in ratios appropriate for small oligomers. These constraints can significantly enhance the ability to resolve minor species (and also the accuracy of the results for the major species).

The aggregation mass of NP-10 is determined by DCDT+ and Svedberg methods. The results are shown below:

C	C0	s	M, DCDT+	M, Svedberg
3.1E-04	0.23	1.314	98.7	75.41
3.5E-04	0.327	1.326	77.39	76.13
4.0E-04	0.376	1.352	93.85	90.21
4.0E-04	0.38	1.37	77.7	68.7
4.5E-04	0.488	1.419	78.37	66.08
5.0E-04	0.669	1.439	89.95	63.28
5.5E-04	0.69	1.434	71.31	

Taking an average aggregation mass (denoted as M) over the measured concentrations, two averages could be obtained for DCDT+ and Svedberg methods, respectively. The average aggregation masses are 83.9 KDa by DCDT+ and 73.3 KDa by Svedberg. From the plot of aggregation masses from DCDT+ and Svedberg as functions of concentration, it is clear that the results by Svedberg have less fluctuation than those by DCDT+.

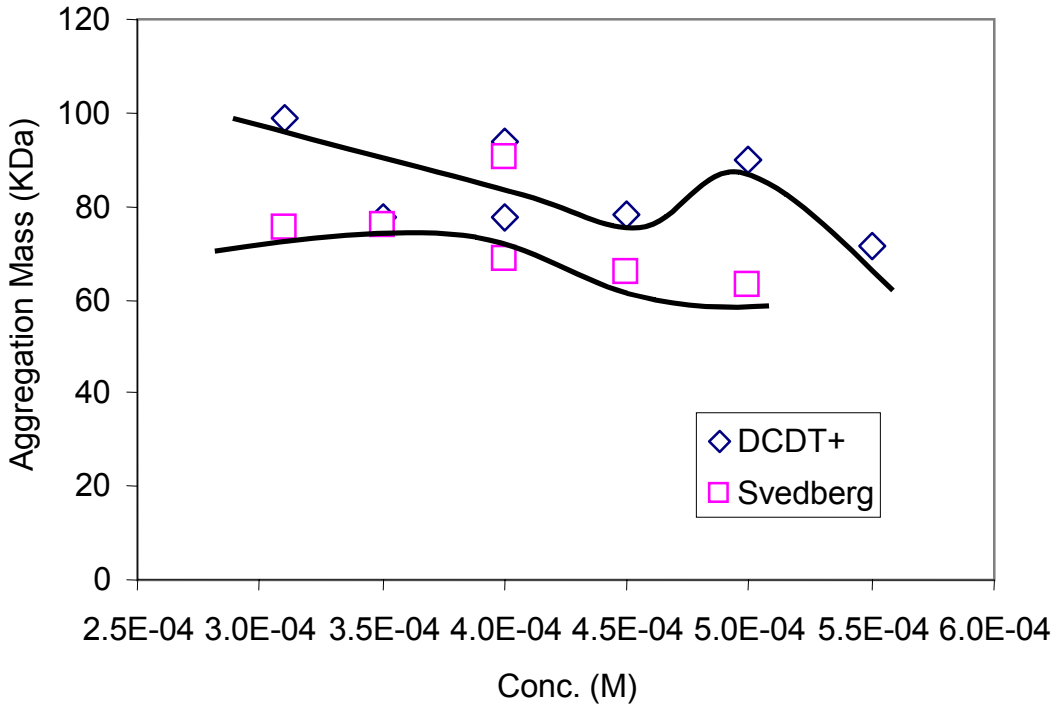


Figure 9. Aggregation masses from DCDT+ and Svedberg as a function of concentration

From the average aggregation masses by DCDT+ and Svedberg, the aggregation number is calculated by dividing the average aggregation masses by molecular weight. They are 127 by DCDT+ and 111 by Svedberg. The result by Svedberg is closer than DCDT+ to the results from Light Scattering.

Although Svedberg is more reliable than DCDT+, this software also has some shortcomings. DCDT+ uses only limited results to get the final results while Svedberg could be applied in the whole range. However, it is possible that no result comes out of Svedberg, i.e., no convergence. As mentioned before, back-diffusion effect due to small molecular weight is responsible for such failures.

4. SEDFIT software

The last software to be introduced is SEDFIT. Although this software has not been applied to our practical analysis, it is claimed that this software is more powerful than others. First, this software treats the results with continuous size-distributions with many known variants for sedimentation velocity analysis with maximum entropy regularization. Second, this software has the most analytical models including discrete non-interacting species, self-associating systems (1-2, 1-3, 1-2-4, 1-4-8), non-ideal sedimentation apparent sedimentation coefficient distribution, ls-g*(s) and van Holde-Weischet analysis G(s) (both for absorbance and interference data). Third, this software makes all sedimentation velocity models for **direct** boundary modeling with algebraic noise elimination. Forth, the software could also be used to analyze data from sedimentation equilibrium experiments by continuous size-distribution models.

The advantage of this software is:

1. Back diffusion effect is taken into account in this case. The outer fitting limit does not need to be set before the bottom to cut off the back-diffusion from the bottom. In principle, it is not

necessary and should not be done when dealing with small molecules that show a significantly larger back-diffusion. In this case, the back-diffusion does contain significant information and should not be ignored.

2. More parameters such as partial specific volume, density, viscosity with unit as poise, **frictional ratio** is calculated by this software. Thus the aggregation mass, sedimentation coefficient and even the shape of micelle can be obtained by SEDFIT.

3. If the surfactant-polymer interaction is to be investigated, the software could also provide 1s-g*(s) in a simple way. Surfactant-polymer combinations usually form large particles where diffusion is negligible. The application of the least-square direct boundary model ls-g*(s) analysis has many similarities to the c(s) analysis, but it is much simpler because of the absence of deconvolution of diffusion and as a result it gives only much lower revolution. This is inherent in any g*(s) model.

From the above discussion, the Svedberg and SEDFIT softwares are found to be better than the other two softwares for analyzing the sedimentation velocity. It is planned to use them for future investigations. The preliminary results indicate that analytical ultracentrifuge is a novel and powerful technique for studying mixed surfactant systems.

SUMMARY AND CONCLUSIONS

Analytical ultracentrifugation is applied for the investigation of surfactant micelles. Work has been completed in the following areas:

1. To obtain accurate results, partial specific volume of NP-10 is calculated using the Helmut Durchschlag and Peter Zipper's method. The result is very close to that obtained experimentally for Triton-100 which has chemical-structure similar to NP-10.

2. Four softwares, OptimaTM XL-A/XL-I data analysis software, DCDT+, Svedberg and SEDFIT, are introduced for the analysis of the sedimentation velocity experimental data. The first three software have been applied to obtain the sedimentation coefficient and aggregation mass. Aggregation numbers obtained are 209, 127, 111 respectively. The last one is closest to the result from light scattering tests.

3. The reason why these three software give different results are given below.

   3.1 OptimaTM XL-A/XL-I data analysis software sets partial specific volume for all substances as that of protein. However, the partial specific volume of NP-10 is much different from that of protein. The OptimaTM XL-A/XL-I data analysis software uses Gaussian distribution to obtain the final result. The resolution of Gaussian distribution is poor. Back diffusion effect can not be handled by this software.

   3.2 DCDT+ has a better resolution than OptimaTM XL-A/XL-I analysis software due to three reasons. First, the partial specific volume and solution density are inputs to reduce the computational error. Second, this software directly fits the dc/dt curves [rather than g(s*)] to obtain the sedimentation coefficient and aggregation mass. Third, the software adopts the modified Fujita-MacCosham function which is the approximate analytical solutions of

Lamm equation. However, the maximum scan number is 99 which yields inaccurate results. The back diffusion effect is not included in the design of this software either.

3.3 Svedberg is better than DCDT+ in that all data can be treated in analysis. The resolution is better than that of DCDT+. Sometimes it is unable to obtain result due to back diffusion effect.

Analytical ultracentrifuge is shown to be powerful for investigating interactions in surfactant mixtures and surfactant-polymer mixtures for enhanced oil recovery processes because it can distinguish individual components and different types of aggregates in complex systems. Also, the pressure generated by centrifugal force can be used to investigate the effect of pressure in deep oil well on the micellization of surfactant mixtures and surfactant-polymer interactions.

FUTURE PLANS

* Apply SEDFIT to the analysis of sedimentation velocity experiment data of NP-10.
* Measure partial specific volumes of each surfactant and surfactant mixtures by digital densiometer.
* Compare hydrodynamic data of surfactant at low concentrations (around several times CMC) with those at high concentrations (around hundred times CMC).
* Apply analytical ultracentrifuge technique to surfactant mixtures.
* Obtain mixing ratio of each surfactant component over the other in mixed micelles by ultra-filtration experiments.
* Perform sedimentation equilibrium experiment to observe the interaction between surfactant micelles and polymers.

* Utilize dynamic light scattering to calculate hydrodynamic radius and diffusion coefficient of micelles.

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