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UNIVERSITY OF OKLAHOMA GRADUATE COLLEGE

:

MONOMERIC, DIMERIC, AND POLYMERIC CATIONIC SURFACTANTS

A Dissertation SUBMITTED TO THE GRADUATE FACULTY in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

By

JING ZHAO

Norman, Oklahoma

1997

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MONOMERIC, DIMERIC, AND POLYMERIC CATIONIC SURFACTANTS

A Dissertation APPROVED FOR THE DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY

BY

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Abstract

This dissertation deals with three types of cationic surfactants, i.e., monomeric, dimeric and polymeric surfactants.

Dimeric surfactants, which are also referred to as gemini or bipolar surfactants, are made up of two identical amphiphilic moieties connected by a spacer near the head group. Most of the studies published so far are concerned with dimethylalkylammonium halide type which are referred to as m-s-m, 2X- surfactants, where s and m are the carbon numbers of the alkanediyl spacer and of the alkyl chain of the hydrocarbon chain, respectively, and Xis the halide counterion. One of the interesting properties of the dimeric surfactants is their co-micellization with conventional surfactants. Synergism was reported for the mixed dimeric and conventional surfactant systems. In chapter 2 and 3 of this dissertation, the study of binary mixed monomeric and dimeric surfactant systems is described. Five bis(quaternary ammonium bromide) surfactants (m-s-m 2Br⁻), namely 12-2-12, 14-2-14, 16-2-16, 16-4-16 and 16-6-16 were synthesized, and a series of conductivity measurements were performed to obtain the Krafft temperatures and cmc's of all five pure dimeric surfactants and their mixtures with cetyltrimethylammonium bromide (CTAB).

Another subject of this work in chapter 4 is the binding of chromate anions by polymeric surfactants, namely polyethyleneimine (PEI), hexyl PEI and lauryl PEI. PEI, one of the most widely studied polyelectrolytes, is known to be a highly branched water-soluble polyamine of variable molecular weight. It is believed to contain primary, secondary, and tertiary amine groups in the ratio of approximately 1:2:1. Owing to its cationic character, in aqueous solution PEI exhibits a strong affinity to anionic materials, including organic and

inorganic anions and polyanions. Hexyl PEI and lauryl PEI were synthesized in this work from PEI and alkyl bromide. A series of ultrafiltration experiments were then performed in which chromate ions were bound by PEI, hexyl PEI and lauryl PEI at various pH values and chromate to EI ratios.

Chapter 1

Overview

1.1 General Consideration

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Surfactant is an abbreviated term for surface-active agent. It is defined [1] as a substance that, when present at low concentrations in a system, has the property of adsorbing onto the surface (or interface) of the system and thereby altering the free energy of that surface (or interface). The term "interface" indicates a boundary between any two immiscible phases, e.g., liquid-liquid, liquid-solid, solid-gas, or liquid-gas. The term "surface" here denotes an interface where one phase is a gas, usually air. It has been known for many years that the physical, chemical, and electrical properties of matter present on boundaries are different from those in the bulk phase. Surfactants often make these differences more significant. Surfactants are some of the most common chemical products used in our daily lives. Because of the scientific and commercial importance, many investigators have done extensive research on different aspects of surfactants.

This dissertation deals with several types of cationic surfactants. An overview of the subject matter will be presented in this chapter followed by detailed descriptions of each system studied in subsequent chapters. Sections 1.2.1 and most of section 1.2.2 are based on my previous writing [2].

1.2 Monomeric Surfactants

A surfactant molecule has a characteristic structure which is said to be amphipathic. The molecule, shown in Figure 1.2-1, consists of two structural portions, one being a lyophobic group (the tail portion) which has little attraction for water, the other one being a lyophilic group (the head portion) which is attracted by water. When a surfactant is dissolved in water, the lyophilic group has the tendency to get into the solvent interior and the lyophobic group has the tendency to get away from the solvent phase. This is what makes the surface-active agent adsorb on the phase boundaries. When this happens, the surface energy is lowered.



Figure 1.2-1 Schematic structure of a surfactant molecule.

1.2.1 Micellization

Micellization is a very important property of surfactants. Thousands of papers have been published since McBain pointed out this phenomenon decades ago [3]. Both the physical and the chemical properties of surfactants have been studied by numerous researchers. It has been found that surfactant molecules in aqueous solutions exhibit a striking characteristic when quantitative data on many of their physical properties are



Figure 1.2-2 Physical properties curves for surfactants



Figure 1.2-3 The process of micellization.

3

plotted against concentration. Figure 1.2-2 is a schematic illustration of the dependence of conductivity, surface tension, osmotic pressure, and high-frequency conductivity on concentration [4-8]. The most important feature in Figure 1.2-2 is a break point in each of the curves. The concentration corresponding to this break point is called the "critical micelle concentration" (cmc). It has been generally recognized that when the concentration is below the cmc, the surfactant molecules exist as monomers, while the molecules become aggregated when the concentration is above the cmc. The aggregated structures are called micelles. The structure of a typical micelle is shown schematically in Figure 1.2-3.

1.2.2 Micelle Shape and Size

It is now known that there are many kinds of micelles. Based on their shape, they are referred to as spherical, ellipsoidal, disk-like, rod-like, etc. The spherical and rod-like micelles are the mostly common types in aqueous solutions of surfactants [9-12]. In most surfactant solutions, spherical micelles are formed just above the cmc.

The major factors that affect the value of the cmc and the size of the micelles are the nature of the polar group, the length and the structure of the hydrophobic chain, and the concentration of added salts [1, 12]. For solutions of ionic surfactants, the micelle size and shape may show an abrupt change at a certain concentration of salt. When the salt concentration is above a threshold value, rod-like micelles form because the presence of salt ions near the polar heads of the surfactant molecules decreases the repulsion force between the head groups. A reduction in the repulsion makes it possible for the surfactant molecules to approach each other more closely and form larger aggregation. A large extent of aggregation requires much more space for the hydrophobic chains. The limitation of the small volume of the spherical micelle core makes it necessary to change to the rod-like micelle, which has a larger volume/surface ratio than the spherical micelle. The existence of rod-like micelles was inferred from light scattering experiments [13-16] and confirmed by electron microscope [17-19].

Rod-like micelles are also called worm-, or thread-like micelles. In general they are all cylindrical micelles. Surfactant solutions with spherical micelles always have a low viscosity. On the other hand the surfactants solutions with large-sized micelles such as cylindrical micelles can be very viscous at very low concentration. This high viscosity can be related to the three-dimensional supramolecular structures, or networks, the cylindrical micelles form in the solutions. The networks of entangled cylindrical micelles was observed by cryo-electron microscopy [20]. A schematic sketch of an entanglement network is shown in Figure 1.2-4. It is generally assumed that the effective network points which are responsible for the elastic behavior are due to their entanglements.



Figure 1.2-4 A schematic drawing of an entanglement network from long cylindrical micelles [21].

1.2.3 The effect of hydrocarbon chain length on the critical micelle concentration (cmc) It is well known that one of the most important factors determining the cmc of surfactant is the number of carbon atoms in the hydrocarbon chain [22]. In aqueous solution, the cmc decreases with the increase of the number of carbon atoms in the hydrophobic chain. The dependence of the cmc on the number of the carbon in the hydrophobic group can be expressed by the equation

$$\log_{10}CMC = A - Bm \tag{1.2-1}$$

where A and B are constants for the particular homologous series and temperature.

The values of A are approximately constant for homologs of different numbers of carbon atoms in the hydrocarbon chain and vary with the kinds and number of ionic groups or substituents in the hydrocarbon chain. The values of B, however, are approximately equal to $\log_{10}2$ for all hydrocarbon chain salts having one ionic group, but vary with the number of hydrophilic groups, including nonionic agents.

Generally this relationship is applicable only when the number of carbons in the hydrocarbon chain is smaller than 16. When the number of carbons exceeds 16, however, the cmc no longer decreases so rapidly with the increase in the length of the chain. When the chain length exceeds 18, the cmc remains substantially unchanged with further increases in methylene groups [1]. This may be due to the coiling of these long chains in water.

1.2.4 The effects of added salts on the cmc

1

When we talk about the effects of salts on the cmc, normally we mean the effect of the counterions. Generally the concentration and the number of charges of the counterions are the most important. It has been found out that the logarithm of the cmc changes linearly with the logarithm of the concentration of counterion C_i [22]

$$\ln CMC = -K_i \ln C_i + \text{const}$$
(1.2-2)

where K_i is an experimental constant for a particular surfactant, electrolyte and temperature with a value of about 0.4-0.7 [23]. K_i is actually the ratio of the number of counterions to long-chain ions in the micelle and is always less than unity. For surfactants which have two ionic groups at one end of the hydrocarbon chain, the slope is twice as great.

$$\ln CMC = -2K_i \ln C_i + \text{const}$$
(1.2-3)

For a 1:1 type surfactant solution at its cmc with no extra salt added, C_i equals to the cmc. For a 2:1 type, however, C_i equals to twice of its cmc.

1.3 Dimeric Surfactants

!

Dimeric surfactants, which are also referred to as gemini [24] or bipolar surfactants [25], are made up of two identical amphiphilic moieties connected by a spacer near the head group as shown in Figure 1.3-1 [26]. Various types of spacer groups, flexible ones such as polymethylene, short polyoxyethylene, heteroatomic, and rigid ones such as xylylene or vinylene di-p-phenylene(stilbene derivatives) [26], have been used. Most of the studies published so far are concerned with dimethylalkylammonium halide type which are referred

to as m-s-m, 2X- surfactants, where s and m are the carbon numbers of the alkanediyl spacer and of the alkyl chain of the hydrocarbon chain, respectively, and X- is the halide counterion. These surfactants are formally the dimers of the quaternary ammonium surfactants with two unequal chains $C_mH_{2m+1}(C_{s/2}H_{s+1})N^+(CH_3)_2X^-$. That is where the name dimeric surfactant came from.



Figure 1.3-1 Schematic representation of a dimeric surfactant.

One of the most important properties of all kinds of surfactants, including both conventional surfactants and dimeric surfactants, is the formation of micelles when the solution is above the cmc. The formation of micelles in aqueous solutions of dimeric surfactants has been investigated in detail [27-29, 40]. Generally, it has been found that the cmc's of dimeric surfactants are at least one order of magnitude smaller than those of the corresponding monomeric surfactants [26].

The microstructure of dimeric surfactants in aqueous solutions have been investigated by cryo-transmission electron microscopy (cryo-TEM). The direct visualization of the freeze-fractured solution of dimeric surfactants 12-s-12 and 16-s-16 revealed that thread-like micelles were clearly observed in the micrographs of 12-2-12 2Br⁻ and 7% 12-3-12 2Br⁻, although the length of the micelles were much shorter for 12-3-12 2Br⁻. The 12-4-12 2Br⁻

, 12-8-12 2Br⁻, 12-10-12 2Br⁻ and 12-12-12 2Br⁻ solutions only show the presence of densely packed spherical or spheroidal micelles. For even longer spacers such as 16 or 20, spherical vesicles, often double-walled and some with defects, were observed [27-29]. Therefore, the microstructures of 12-s-12 2Br⁻ were mainly determined by the length of its spacer.

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Similar to 12-2-12 series, micrographs of 16-s-16 2Br⁻ series showed that the microstructures of 16-s-16 2Br⁻ also changes with the length of its spacer. Unilamellar vesicles were found to coexist with bilayer membrane fragments and thread-like micelles in solutions of 16-3-16 2Br⁻, whereas only thread-like micelles were present in solutions of 16-4-16 2Br⁻ and spherical micelles in solutions of 16-6-16 2Br⁻ [29].

One of the interesting properties of the dimeric surfactants is its co-micellization with conventional surfactants. Synergism were reported for the mixed dimeric and conventional surfactant system. The studies for the mixed micellization of 12-2-12 and its corresponding monomeric surfactant dodecyltrimethylammonium bromide (DTAB) by using cryo-TEM showed a progressive breakdown of the thread-like micelles and their transformation into mixed spherical micelles, upon addition of DTAB to the dimeric solution.

The unique properties of dimeric surfactants may lead to potential new applications. The solubility of the dye trans-azobenzene by micellar solutions of m-s-m $2Br^-$ with s = 2 to 12 and m = 8 to 16 has been investigated [30]. The inhibitory action of dimeric quaternary ammonium surfactants, particularly of the 10-s-10 $2Br^-$ series, on photosynthesis [31] and bacterial activity [32] has also been studied. Since dimeric surfactants often have better

wetting ability for various materials [33] than conventional surfactants, a large number of dimeric surfactants with various head groups and spacers were synthesized and tested. The study by Tanaka *et al.* [34] also found out that the use of a dimeric sodium sulfonate surfactant had better effect in electrokinetic chromatography than the often used sodium dodecyl sulfate.

In summary, the dimeric surfactants and probably their higher homologs, such as trimeric and pentameric surfactants, are very interesting in both basic research and industrial applications.

1.4 Polymeric Surfactants

Another kind of surfactant is polymeric surfactant. In view of the steadily increasing importance of polymeric surfactants in technical applications, there has been a growing interest in their physicochemical properties, especially in relation to a better understanding of the mechanism in these applications [35].

One of the most widely studied polyelectrolytes is polyethyleneimine (PEI). PEI is known to be a highly branched water-soluble polyamine of variable molecular weight. It is believed to contain primary, secondary, and tertiary amine groups in the ratio of approximately 1:2:1 [36]. There is experimental evidence that branching sites are separated mainly by secondary amine groups, with about one branch for every 3 to 3.5 nitrogen atoms within a linear chain [37]. Owing to its cationic character, in aqueous solution PEI exhibits a strong affinity to anionic materials, including organic and inorganic anions and polyanions. The driving force for binding includes both the electrostatic attraction between opposite charges and the increase in solvent interaction energy between hydrophobic

regions of the polymer and the organic moiety. Kinetic and thermodynamic studies reveal that counterions can bind cooperatively to form polyelectrolyte complexes [38]. Obviously, the stoichiometry of the complexation of PEI with anions depends on the degree of protonation, i.e., the pH of the PEI solution.

Polyethyleneimine and its derivatives have a wide application in industry [39]. In rubber industry, polyethyleneimine can be used to control coagulation of SBR latex to eliminate the loss of fines; they are also used to improve adhesion of rubber tire cord. In adhesive systems such as coatings on glass fibers and synthetic fibers, PEI is also very useful due to its polarity and reactivity. In paper-making, polyethyleneimines are used as wet-strength additives. PEI can also be used in the synthesis of ion-exchange resins, water purification and clarification of process effluents. Another field of commercial application of PEI and its derivatives is apparently related to their ability to form complexes with heavy metal ions [35]. In electroplating processes the gloss of zinc or nickel plated surfaces is markedly improved by the presence of these polymers, or they can be used to bind the heavy metal ions in waste water to make the polluted water purified.

The polyethylenimines can be alkylated to increase their hydrophobicity. Hexyl PEI and lauryl PEI are two of the alkylated PEIs synthesized in this work. The binding of chromate with PEI, hexyl PEI and lauryl PEI were studied and will be discussed in chapter 4.

1.5 Systems Studied in this Work

In chapters 2 and 3 of this dissertation, the study of binary mixed monomeric and dimeric surfactant systems is described. Five bis(quaternary ammonium bromide) surfactants (m-

s-m 2Br⁻), namely 12-2-12, 14-2-14, 16-2-16, 16-4-16 and 16-6-16 were synthesized. and the properties of their mixtures with cetyltrimethylammonium bromide (CTAB) will be discussed in the following two chapters. Even though many publications can be found concerning both basic properties and applications of m-s-m [27-29, 40], a very important property of this type of dimeric surfactant, the Krafft temperature, i.e., the temperature at which the solubility of the surfactant precipitates increases dramatically, seemed to be ignored by many investigators. Since only when the experiments are performed above the dimeric surfactant's Krafft temperature, the solution is homogeneous and the data collected are equilibrium values. However, many data of m-s-m such as cmc, ionization degree, micellization number etc. published so far [26-29, 40] were all obtained at 25 °C without first measuring the Krafft temperature. Because the Krafft temperatures of many surfactants are much higher than room temperature, it is essential to determine their values for newly synthesized surfactants. Therefore, a series of conductivity measurements were performed in this work to obtain the Krafft temperatures of pure dimeric surfactants 12-2-12, 14-2-14, 16-2-16, 16-4-16, 16-6-16 and their mixtures with CTAB.

Since the cmc is one of the most basic and important properties of the surfactants, and many of the published cmc data for dimeric surfactant m-s-m are not reliable due to the incorrect experimental temperature [40], the cmc for the five pure m-s-m and their mixtures with CTAB were obtained in this work through conductivity measurements. The detailed results and discussion for the cmc experiments can be found in chapter 3.

Another subject of this work is the binding of chromate anions by polymeric surfactants PEI, hexyl PEI and lauryl PEI. As discussed in the above section, PEI is a very common polymer in industry and is commercially available with affordable price. Hexyl PEI and Lauryl PEI were synthesized in this work from PEI and alkyl bromide. Micellar-enhanced ultrafiltration has been developed for removing metal ions and soluble, low-molecular weight organics from water [41-44]. When the polluted water with metal ion bound surfactant passes though a membrane with the molecular weight cut-off small enough to block most of the micelles in the retentate side, a pure permeate could be obtained. Because the cmc's of polymeric surfactants are essentially zero, they may be propitious in micelle-enhanced ultrafiltration. Besides the advantage that no polymeric molecules can pass through the membrane, extremely low trace quantities of highly toxic or valuable multivalent metal ions can be removed by using low concentrations of polymers.

A series of ultrafiltration experiments were performed by binding chromate ions by PEI, hexyl PEI and lauryl PEI at various pH values. Detailed experimental data and discussion can be found in chapter 4.

Bibliography

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- 1. Rosen, M. J, Surfactants and Interfacial Phenomena, Wiley Interscience, New York (1978).
- 2. Jing Zhao, M. S. thesis, University of Oklahoma, 1992.
- 3. Fredric M. Menger, Acc. Chem. Res., 1979, 12, 111.
- Howell, O. R., and Robinson, H. G. B., Proc. Roy. Soc. (London), 1936, A155, 386.
- 5. Powney, J., and Addison, C. C.: Trans. Faraday Soc., 1937, 33, 1243.
- 6. Hess, K., Philippoff, W., and Kiessig, H.: Kolloid-Z., 1939, 88, 40.
- 7. Hess, K., and Suranyi, L. A.: Z. physik. Chem., 1939, A184, 321.
- Stauff, J.: Z. physik. Chem., 1939, A185, 45; 1940, A187, 119; Kolloid-Z.
 1939, 89, 224.
- 9. Florence, A. T., Prafitt, R. T., J. Phys. Chem., 1971, 75, 3554.
- 10. S. Ozeki and S. Ikeda, J. Colloid Interface Sci., 1980, 77, No. 1, 219.
- 11. Debye, P., and Anaker, E. W., J. Phys. Colloid. Chem., 1951, 55, 644.
- 12. Stigter, D., and Mysels, K. J., J. Phys. Chem., 1955, 55, 45.
- 13. S. Hayashi and S. Ikeda, J. Phys. Chem., 1980, 84, 744-751.
- 14. S. Ikeda, S. Ozeki, and M. Tsunoda, J. Colloid Interface Sci., 1980, 73, No.1, 27.
- 15. S. Ozeki and S. Ikeda, J. Colloid Interface Sci., 1981, 87, No.2, 424.
- T. Imae, R. Kamiya, and S. Ikeda, J. Colloid Interface Sci., 1985, 108, No.1, 215.
- 17. B. M. Fung, D. L. Mamrosh, E. A. O'rear, C. B. Frech, and J. Afzal, J. Phy. Chem., 1988, vol. 92, No. 15.

- 18. T. Imae, R. Kamiya, S. Ikeda, J. Colloid Interface Sci., 1984, 99, 300.
- 19. P. K. Vinson, J. Colloid Interface Sci., 1989, Vol. 133, No. 1.
- T. M. Clausen, P. K. Vinson, J. R. Minter, H. T. Davis, Y. Talmon, W. G. Miller, J. Phys. Chem. 1992, vol. 96, No. 1, 474-484.
- 21. H. Hoffmn, in "Structure and Flow in Surfactant Solutions", Ed. C. A. Herb and R. K. Prud'homme, ACS symposium 578, chapter 1, Washington D. C., 1994.
- 22. K. Shinoda, "Colloidal Surfactants", chapter 1, New York, 1963.
- 23. I. J. Lin and P. Somasundaran, J. Colloid Interface Sci., 1971, 39, 731.
- 24. F. M. Menger, and C. A. Littau, J. Am. Chem. Soc., 1993, 115, 10083; J. Am. Chem. Soc., 1991, 113, 1451.
- 25. J. H. Fuhrhop, and D. Fritsch, Acc. Chem. Res., 1986, 19, 130.
- 26. R. Zana in "Spec. Surfactants", Ed. I. D. Robb, Blackie, London, UK, 1997, chapter4, pages: 81-103.
- 27. R. Zana and Y. Talmon, Nature, 1993, 362, 228.
- 28. D. Danino, A. Kaplun, et al. in "Structure and Flow in Surfactant Solutions", Ed. C.A. Herb and R. K. Prud'homme, ACS symposium 578, Washington D. C., 1994.
- 29. D. Danino, Y. Talmon, and R. Zana, Langmuir, 1995, 11, 1448.
- 30. F. L. Devinsky, I. Lacko, and T. Iman, Acta Fac. Pharm., 1990, 44, 103 and J. Colloid Interface Sci., 1991, 143, 336.
- 31. K. Kralova, and F. Sersen, Tenside Surf. Det., 1994, 31, 192.
- 32. T. Imam, F. Devinsky, et al. Pharmazie, 1983, 38, 308; F. Devinsky, I. Lacko, et al. Tenside Det., 1985, 22, 10
- 33. Y. P. Zhu, A. Masuyama, and M. Lkahara, J. Am. Oil Chem. Soc., 1990, 67, 459;
 J. Am. Oil chem. Soc., 1991, 68, 268.
- 34. M. Tanaka, T. Ishida, et al. J. Chromatogr., 1993, 648, 469.
- 35. D. Horn, polyethyleneimine

- 36. G. M. Lukovkin, V. S. Pshezhetsky, and G. A. Murtazaeva, *Europ. Polym. J.*. 1973, 9, 559-565.
- 37. C. R. Dick and G. E. Ham, J. Macromol. Sci. Chem., 1970, A4 (6), 1301-1314;
 G. M. Lukovkin, V. S. Pshezhetsky, and G. A. Murtazaeva, Europ. Polym. J., 1973, 9, 559-565.
- 38. H. Terayama, J. Polym. Sci., 1952, 8, 243-253; A. S. Michaels, Ind. Eng. Chem., 1965, 57, 32-40.
- 39. L. E. Davis and R. D. Deanin, SPE Journal, 1968, vol. 24, 59-61.
- 40. R. Zana, M. Benrraou and R. Rueff, Langmuir 1991, 7, 1072-1075.
- 41. Tucker, E. E.; Christian, S. D.; Scamehorn, J. F.; Uchiyama, H.; Wen, G. in Removal of Chromate from Aqueous Streams by Ultrafiltration and Precipitation, Sabatini, D. A.; Knox, R. C., Eds.; "Transport and Remediation of Subsurface Contaminants", 1992.
- 42. Dunn JR, R. O.; and Scamehorn, J. F. Sep. Sci. Technol. 1985, 20(4), 257-284.
- 43. Dunn JR, R. O.; and Scamehorn, J. F., Christian, S. D. Sep. Sci. Technol. 1987, 22(2&3), 763-789.
- 44. Christian, S. D.; Bhat, S. N.; Tucker, E. E.; Scamehorn, J. F.; El-Sayed, D. A. AIChE J. 1988, 34, 189.

Chapter 2

Mixtures of Monomeric and Dimeric Cationic Surfactants I. Study of Krafft temperature

2.1 Theory

2.1.1. Dimeric Surfactants

<u>2.1.1.1</u> Structure of dimeric surfactants. Dimeric surfactants, which are also called twin surfactants, are made up of two identical amphiphilic moieties connected at the proximity of the head groups by a spacer group which can be hydrophilic or hydrophobic, rigid or flexible. The most common type of dimeric surfactants are bis(quaternary ammonium) salts [1]. The structure of these cationic surfactants is illustrated in the following:

+ +
Br⁻ (CH₃)₂N⁻ (CH₂...Y...CH₂) - N (CH₃)₂ Br⁻
$$\begin{vmatrix} s \text{ carbon atoms } \\ R \end{vmatrix}$$

where $R = C_m H_{2m+1}$, $C_m H_{2m+1} CH_2 CO_2$, or $C_m H_{2m+1} CO_2 CH_2 CH_2$ and $Y = CH_2$, NCH₃, S, or O.

One kind of dimeric surfactant with $R = C_m H_{2m+1}$ and $Y = CH_2$, which is also referred to
as m-s-m, has been studied widely in recent years mainly by Zana's group [2-10]. The structure of m-s-m are shown as below:

Br'
$$(CH_3)_2$$
N - $(CH_2)_s$ - N $(CH_3)_2$ Br'
 $\begin{vmatrix} & & \\ & & \\ & & \\ & & \\ & & C_mH_{2m+1} & C_mH_{2m+1} \end{vmatrix}$

These m-s-m dimeric surfactants, which are also called "gemini" or bipolar surfactants, can be considered as dimers of two quaternary ammonium surfactants $C_mH_{2m+1}(C_{s/2}H_{s+1})N^+(CH_3)_3Br^-$. Their properties are strongly affected by the length of the polyethylene chain (spacer) containing s carbons. This is also the type of dimeric surfactant studied in this work.

It has been shown that dimeric surfactants are better bactericidal agents than the corresponding monoquaternary surfactants [1]. Therefore, many fundamental properties of this type of compounds, such as critical micelle concentration (cmc), degree of micelle ionization, and aggregation number, have been studied [2-12]. It was found that they are superior to the corresponding conventional monomeric surfactants in many properties, such as they have lower critical micelle concentration (cmc), are more efficient in lowering the surface tension of water, have better lime-soap dispersing properties, and are often better wetting agents [13]. Studies were also made on their ability to co-micellize with the corresponding single chain quaternary ammonium surfactants and other surfactants [4, 5, 10]. Besides the goal of lowering the higher cost of pure dimeric surfactants, synergistic effects which were found in many conventional/dimeric surfactant mixtures also make the

study of their mixtures more attractive.

2.1.1.2 Effect of the spacers on the microstructures of dimeric surfactants. In classical surfactants the head groups are distributed uniformly on the surface of the micelles. This layer of head-groups separates the aqueous phase from the micelle hydrophobic core. In dimeric surfactants, however, the distribution of this layer of head-groups largely depends on the length of the spacer. When the spacer is short enough, for example less than 6, it is probably fully stretched at the water-micelle interface [9]. When s increases, it is more difficult for the spacer to remain in contact with water, and it moves to the inside of the micelles instead. As a result of the folding of the spacer in the micelle core, the quaternary ammonium groups get closer to each other. This argument is also applicable to the distribution of the dimeric surfactants on the water-air interface.

The behavior of the 12-s-12 2Br⁻ series of compounds at the air-water interface provides a full support to the above argument [3]. Zana's group has made the surface tension measurement for a series of compounds 12-s-12 2Br⁻ with s value of 3, 4, 6, 8, 10, 12, 14 and 16. The surface excess concentration Γ and the surface area a per bis(quaternary ammonium) surfactant were calculated using the Gibbs equation

$$\Gamma = -1 / (2.30 \text{nRT}) (d\gamma/d\log C)_{\text{T}}$$
 (2.1-1)

and the equation

$$\mathbf{a} = (\mathbf{N}_{\mathbf{A}} \Gamma)^{-1} \tag{2.1-2}$$

where R = 8.32 J mol-1 deg⁻¹, T = 298.15 K with γ expressed in newtons per meter, and n is the number of moles of the substance on the surface.

The plot of the surface area against the number of carbon atoms in the spacer, s, shows that the surface area goes through a maximum with the increase of the space number s, which is shown in Figure 2.1.1-1. This maximum occurs at s equals 10 to 12. After this maximum, the surface area decreases, which implies that the spacer folds away from the water surface. The changes of the spacer at the air-water interface is illustrated in Figure 2.1.1-2.

<u>2.1.1.3 The shape of the micelles formed by dimeric surfactants</u>. The study of the means to control the shape of micelles has always been an important topic in surfactant research of both academic and applied interest, because to a large extent the micellar shape determines many properties, and also some applications, of surfactants in solution. When a surfactant solution is well above the cmc, the shape of the micelles can be predicted by the so called surfactant packing parameter introduced by Israelachvili *et al* [14]. The packing parameter, P, is:

$$\mathbf{P} = \nu/(a_M l) \tag{2.1-3}$$

where v and l are the volume and length of the surfactant hydrophobic moiety, respectively, and a_M is the surface area occupied by a surfactant head-group at the interface between water and the micelle hydrophobic core. v and l can be calculated using Tanford's equations [15]. For a conventional surfactant (one alkyl chain and one head-group), v/l,



Figure 2.1.1-1 Variation of the surface area per surfactant with the spacer carbon number [3].



Figure 2.1.1-2 Schematic representation of the bis(quaternary ammonium) surfactants at the air-water interface: (a) s < 10; (b) $s \ge 10-12$ [3].

*

which is the cross-section of the alkyl chain, is close to 21 A^2 , when the alkyl chain contains 12 or more carbon atoms. The packing parameter has been a tool in understanding the effect of various parameters such as surfactant chain length, branching of the alkyl chain, head-group size, ionic strength, temperature, nature of the counterion, etc., on the shape of micelles of conventional surfactants.

Following the results of the surface area study, it was expected that the length of the spacer must also have a direct effect on the morphology of the micelles, which was inferred from cryogenic transmission electron microscopy (cryo-TEM) experiments [5, 9-10]. Cylindrical and lamellar as well as spherical mesophases were observed for 12-s-12 2Br homologue aqueous solutions. 12-2-12 2Br forms strongly entangled thread-like micelles, and the thread-like micelles are shorter for 12-3-12 2Br. When s increases from 4 to 8, however, only spherical micelles were observed. Therefore, changes in the characteristics and behavior of the dimeric surfactants with the variation of spacers have been observed.

In addition to the change in the shape of the micelles of the 12-m-12 dimeric surfactants with the length of the spacer, the change can also be induced by mixing with monomeric surfactants. When 12-2-12 is mixed with dodecyltrimethylammonium bromide (DTAB), the shape of the micelles changes progressively from thread-like to spheroidal with the increases of the fraction of DTAB [5]. On the basis of the fact discussed above, Zana and his group proposed a new way [4, 8] for controlling the shape of micelles, by linking the amphiphiles at the level of the head-group, thus generating oligomeric (dimers, trimers, tetramers, etc.) amphiphiles and polyamphiphiles. The shape of the micelles in the surfactant solution can therefore be controlled as required by changing the spacer or mixing

with another surfactant.

2.1.2. Precipitation

Precipitation of surfactants from aqueous solutions is very important in applications such as detergency and enhanced oil recovery. Precipitation of anionic and cationic surfactants in oil reservoirs is the basis of an improved waterflooding technology to enhance crude oil recovery [17]. The recovery of surfactants can also be achieved by precipitating the surfactant from surfactant-based separation processes. Even though it can be useful in the petroleum production, precipitation is undesirable in detergency. Considerable effort has been expended to reduce the precipitation so that the detergent will possess high hardness tolerance to permit washing in hard water [16, 17].

Precipitation is generally presented quantitatively in two ways: phase boundary diagrams and Krafft temperature. The Krafft point is the temperature at which the solubility of surfactant increases sharply with increasing temperature [16]. This increase is so sharp that the dissolution temperature of the precipitate is essentially independent of concentration above the critical micelle concentration (cmc). A phase boundary is the minimum or maximum concentration of an additive required to form an infinitesimal amount of precipitate in the aqueous surfactant solution at constant temperature with various surfactant concentrations. A phase diagram of sodium dodecyl sulfate (SDS) precipitated by Ca²⁺ at 30°C is shown in Figure 2.1.2-1 [18]. The boundary separates the diagram into two regimes: one is the part where precipitation occurs at equilibrium, the other is where a clear solution is present. Anionic surfactant precipitation has been studied extensively by Scamehorn's group [14-19]. The minimum concentration of multivalent cation necessary to cause precipitation of the surfactant is called hardness tolerance. Salinity tolerance, however, is defined as the minimum concentration of monovalent cation necessary to cause precipitation of the surfactant. Hardness tolerance can limit the effective cleaning using anionic surfactants in hard water, and is therefore needed to be eliminated by adding some additional builder to the detergent. Salinity tolerance is generally of less importance than hardness tolerance except that surfactant flooding of extremely saline oil reservoirs can be limited by this kind of precipitation.

Figure 2.1.2-2 illustrates an equilibrium between monomer, micelle, and precipitate for a micellar system containing an anionic and a nonionic surfactant, where the anionic surfactant is being precipitated by monovalent counterion [20]. At equilibrium, the solubility product K_{spi} is related to the activities of the surfactant monomer and the counterion by the following equation:

$$K_{spi} = [activity of surfactant monomer][activity of counterion]$$
 (2.1-4)

Therefore, surfactant precipitation can only occur if the product of the surfactant monomer activity and the counterion activity exceeds the solubility product of the surfactant. As a matter of fact, micellization and precipitation are two competitive processes in a surfactant solution above the cmc. At a total constant surfactant concentration, the more easily micelles form and the higher counterion binding is on the micelles, the more difficult it is for precipitation to occur because the surfactant monomer and counterion activity or concentration are reduced. Therefore, the key to decreasing the extent of precipitation at a certain temperature is to enhance micelle formation, which decreases monomer concentration. This purpose can be achieved by adding another surfactant into the system.

Generally, cationic-anionic surfactant pairs can precipitate easily, so the mixing of a



Figure 2.1.2-1 A phase diagram of SDS precipitated by Ca^{2+} at 30°C [16].



Figure 2.1.2-2 Schematic diagram of monomer-micelle-precipitate equilibrium in a ternary anionic surfactant system [18].

cationic and an anionic surfactant should be avoided. An anionic-nonionic or cationicnonionic surfactant system can form micelles more easily than pure anionic or cationic surfactant. This is because the nonionic surfactant hydrophilic groups insert themselves between the anionic or cationic surfactant hydrophilic groups, decreasing electrostatic repulsion between these charged head groups, also reducing charge density and electrical potential at the micelle surface. Therefore, the tendency for the precipitation of ionic surfactants can be reduced by the addition of nonionic surfactants.

2.1.3. Krafft Temperature

In general, the way to reduce surfactant precipitation is to increase micellization so that the activity product of the surfactant monomer and the counterion is reduced. When the total surfactant and counterion concentration is kept constant in the solution, the extent of precipitation has to be reduced by increasing the temperature. Theoretically, the Krafft temperature should be obtained by lowing the temperature of a homogeneous surfactant solution until precipitation occurs. Experimentally, the Krafft temperature measurement is normally performed in an opposite way, i.e., the surfactant solution is first cooled down to cause precipitation, and then heated up gradually until all the precipitates disappear. The reason for doing so can be illustrated by Figure 2.1.3-1 [21], which shows the precipitation phase boundary of an anionic surfactant with calcium as a function of time. Clearly, the phase boundary changes over a long period of time, which indicates that these systems reach equilibrium very slowly. To make the experimental process more efficient, the Krafft temperature is normally obtained by heating the precipitated solution gradually. When a precipitated surfactant solution is heated, the solubility of the surfactant increases with the increase of the temperature. When the temperature is finally close to the Krafft point, the solubility of the precipitates increases dramatically until all precipitates

Precipitation of Surfactant Mixtures



Figure 2.1.3-1 The Ca²⁺/sodium p-(1-methylnonyl)benzene sulfonate precipitation domain at pH 5.5 and 25°C [21].

dissolve at the Krafft point. Visual observation is the method commonly used for determining Krafft temperature [16-20]. A disadvantage of the visual observation is the inaccuracy. Even though the heating process is much faster than the cooling process, the time for reaching equilibrium at a certain temperature still varies for different compounds, sometimes requiring hours. If insufficient time intervals are used in raising temperatures during Krafft temperature measurement, the solution may not have reached equilibrium before the temperature is raised for the next measurement. Therefore the Krafft temperature obtained this way could be higher than the actual Krafft point. To make the measurement more accurate, conductivity measurements were employed in this work for the Krafft temperature determination. During the conductivity measurement, the solublizing process can be monitored by the conductivity reading. When the temperature is raised, the conductivity reading will increases until an equilibrium is reached. With this method, time interval between two temperatures is not necessary to be the same. While it takes only a few minutes to get to equilibrium at some temperatures, it takes as long as more than an hour to reach equilibrium at others. More importantly, quantitative data are obtained for the determination of the physical change in the system, rather than a reliance on the subjective judgement of the experimenter as in visual observation. Some other techniques such as turbidity and UV absorbance can also be used for the Krafft temperature determination. However, conductivity measurement is easier technically compared with the other two methods.

The isothermal phase boundary diagram is a good way of data presentation because the results are easier to model and are more useful, particularly for mixed surfactant systems. However, the Krafft temperature is still one of the most important properties of surfactants which should be obtained before other properties are studied. Unfortunately, this essential point is sometimes ignored. For example, in one of Zana's publications [3], a series of dimeric surfactants was synthesized and the properties such as the cmc, and the degree of micelle ionization were studied. The cmc data were determined at 25°C without determining the Krafft temperature first. In our later discussion it will be shown that the Krafft points for m-s-m are very high except for the 12-s-12 series, and is as high as 45 °C for 16-2-16. The reason that some of the physical measurements at 25°C could be done is just discussed above: after a solution of the dimeric surfactant is made (it has to be heated to boiling to dissolve), it takes a very long time to precipitate. So if the measurement is performed immediately with a freshly made solution, a reasonable reading can be obtained. However, after the solution is left at room temperature for some time, for example overnight, it will turn cloudy and eventually precipitate. The data obtained are not

meaningful because they are not equilibrium values.

Similar to hardness and salinity tolerance, the Krafft temperature of a surfactant system can also be lowered by adding another surfactant. As a matter of fact, a eutectic type of behavior is commonly observed for binary mixtures of precipitating surfactant [17, 20]. Figure 2.1.3-2 and Figure 2.1.3-3 show the Krafft points of a binary mixture of 3- ϕ -decylbenzene sulfonate (3- ϕ -C10 ABS)/4- ϕ -dodecylbenzenesulfonate (4- ϕ -C₁₂-ABS) [22] and a mixture of SDS/N^{α}, N^{α}-dimethyl-N^e-lauroyl lysine (DMLL) [23]. In Figure 2.1.3-2, the Krafft temperatures of both pure surfactants are above 16°C, but the Krafft point is lowered upon the addition of another surfactant, and the Krafft temperature of an equimolar mixture is even lower than 0°C. Figure 2.1.3-3 shows the Krafft temperature of a binary system with or without added salt. Besides the eutectic behavior shown for all three curves, it can also be seen that added counterions will increase all the Krafft temperatures compared with the corresponding pure or mixed surfactants at the same fraction. The more the added counterion, the higher the Krafft temperature is raised.

In summary, for both isothermal (hardness or salinity tolerance) and variable temperature (Krafft temperature) conditions, the use of surfactant mixture always permits considerable manipulation of precipitation behavior over a single surfactant.



Figure 2.1.3-2 Krafft point of an anionic-anionic surfactant mixture $(3-\phi-C_{10}ABS)/(4-\phi-C_{12}ABS)$ [20]

Figure 2.1.3-3 Krafft point of an anionic-amphoteric surfactant mixture (SDS/DMLL).[21]



2.2 Experimental

2.2.1. Materials and Instruments

Cetyltrimethylammonium bromide (CTAB) was purchased from Fisher Scientific and was used without further purification. N, N, N', N' - Tetramethylethylenediamine was purchased from SIGMA Chemicals. N, N, N', N' - Tetramethyl - 1, 6 - hexanediamine and N, N, N', N' -Tetramethyl - 1, 4 -butanediamine were purchased from ACROS Organics. Alkylbromides (1-bromododecane, 1-bromotetradecane, 1-bromohexadecane) were all purchased from Aldrich Chemicals. 98% Cetylpyridinium bromide (CPB) was purchased from Aldrich and was used without further purification. Sodium dodecylsulfate (SDS) and 4-octylbenzenesulfonic acid (SOBS) were all purchased from Aldrich. SDS was at least 99% pure and was recrystalized from water and then from methanol. SOBS was at least 97% pure and was recrystalized first from methanol and then from water.

A Fisher Scientific Isotemp Refrigerated Circulator, Model 901, was used as the water bath for the conductivity measurement. A VWR Scientific Conductivity Meter, Model 2052, and a VWR 515 conductivity dip cell were employed for the conductivity measurements.

2.2.2. Synthesis

Compounds in the m-s-m series (16-2-16, 16-4-16, 16-6-16, 14-2-14 and 12-2-12) were synthesized with alkanediyl- α , ω -bis(dimethylamine) reacting with alkylbromide for s = 2, 4, 6 [3]. The reactions were performed in dry ethanol under reflux for 48 h in the presence of 5-10 % excess of alkylbromide to ensure complete bis-quaternization as much as possible.

$$(CH_3)_2 N \cdot (CH_2)_s - N (CH_3)_2 + 2 Br C_m H_{2m+1}$$



The surfactants were recrystalized in various solvent mixtures (ethanol-ethylacetate and /or acetone-ethylacetate for the dodecyl series; chloroform-ethyl acetate for the hexadecyl series). Normally the solvent in which the surfactant has small solubility was first added to the crude surfactant. Then another solvent which dissolves more surfactant was added to the above mixture until all the surfactant dissolved. The surfactant-solvent mixture was heated up while solvent was added to the solution. The dissolved surfactant solution was coole to room temperature, then moved to the refrigerator to make the precipitation more complete. The recrystalization was normally repeated three times.

Table 2.2-1 Elemental Analysis of m-s-m

m-s-m	Analysis	С	N	Br	н
16-2-16	Theory	62.79	3.85	21.99	11.37
	% Found	60.65	3.83	22.92	11.08
14-2-14	Theory	60.88	4.18	23.82	11.12
	% Found	59.5	4.28	25.39	11.26

The purity of 16-2-16 and 14-2-14 were checked by elemental analysis, and the results are given in Table 2.2-1.

All products were checked by nuclear magnetic resonance (NMR) spectroscopy. The samples were run in CDCl₃. As an example, the proton NMR spectrum for 16-4-16 is shown in Figure 2.2-1. Nine peaks are assigned for the protons in this compound: alkyl chain N-CH₂; β -CH₂; γ -CH₂; δ -CH₂; CH₂ in the middle of the chains; ω -CH₃, spacer N-CH₂; spacer CH₂; head group N-CH₃. ¹H-NMR (500 MHz, CDCl₃): δ [ppm] = 0.87 (t, 6H); 1.22-1.26 (m, 44H); 1.35 (m, 4H); 1.50-1.55 (m, 4H); 1.75-1.78 (m, 4H); 2.20-2.22 (m, 4H); 3.23 (s, 12H); 3.26-3.28 (m, 4H); 4.05-4.08 (m, 4H). The integrated spectra gave the expected proton contents. If there is a rearrangement during the reaction to prepare the dimeric surfactants, the compound (C_mH_{2m+1})₂(CH₃)N⁺(C_sH_{2s})N⁺(CH₃)₃ 2Br⁻ may form as an impurity. However, the NMR spectrum shows that the amount of this possible compound is negligible.

2.2.3. Conductivity Measurement

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2.2.3.1 Samples preparation. 3 mM CTAB and dimeric surfactant stock solutions were made first and kept in a 40°C water bath. A set of 10 mL, 3 mM samples were then made by mixing the above CTAB and dimeric surfactant stock solutions with the required fraction in caped plastic tubes, which do not break in the freezer. The 10 mL samples were then kept in ice-water. If no precipitation happened overnight or after a few days, the sample would be removed to a freezer at -18 °C for precipitation (normally it takes a few hours for any sample to precipitate in a freezer). Freezer-precipitated samples would then be warmed up in a cold room at 4 °C until completely aqueous samples with precipitation were obtained.



Figure 2.2-1 ¹H-NMR spectrum of 16-4-16 2Br⁻.

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2.2.3.2 Conductivity measurement. The precipitated samples prepared as described above were transferred to round bottom glass tubes. Then the conductance of each sample was measured while it was submerged in a constant-temperature water bath. Since the water bath temperature had to be adjusted manually, the exact temperature would be read from a thermometer inserted in the water bath. A VWR digital conductivity meter, Model 2052, was employed to perform the conductivity measurements in this work. The direct reading from the conductivity meter was conductance. The conductance of water, 1.3 μ S, was subtracted from all the readings. The resulting conductance value was multiplied by the cell constant of the conductivity cell used, 10.46 cm⁻¹, to give a conductivity value. The cell constant, which can be read directly from the conductivity meter after the calibration, is the conducting path 1 (distance between the plates) divided by the effective cross sectional area A, namely I/A.

During the determination of Krafft temperature, the temperature was raised from low to high. The conductance reading was checked every 2-5 minutes until the reading stayed unchanged. Then the temperature was raised by 1-2 degrees. Every time the reading was checked, the conductivity probe was moved up and down to stir the sample. For the purpose of comparison, the conductivities of three samples, 16-4-16, CTAB and CPB, were also measured with temperatures decreasing. In these experiments, it was very difficult for the equilibrium to be reached around the Krafft points before lowering the temperature for the next reading, because it takes a longer time for a surfactant to precipitate than to dissolve. Therefore a lower Krafft point was obtained by this method for CTAB and CPB, and the Krafft point could not be obtained for 16-4-16.

2.3 Results and Discussion

2.3.1. Krafft Temperature of pure m-s-m dimeric surfactants

The krafft temperature is the temperature at which the solubility of hydrated surfactant crystals increases sharply with increasing temperature. This increase is so sharp that the solid hydrate dissolution temperature is essentially independent of concentration when the solution is above the cmc. Theoretically only an infinitesimal amount of crystals exist in the solution when the solution reaches equilibrium at the Krafft temperature. Therefore the solution at Krafft point can be considered homogeneous. The Krafft temperature is such an important property for a surfactant that it should be determined before all other properties are studied.

2.3.1.1 Cooling time. Krafft temperature is a very significant property in the application of surfactants. Only when the surfactant is used above its Krafft temperature, can the solution be maintained homogeneous. Some surfactants can precipitate from the solution in a short time when it reaches the Krafft temperature, whereas some surfactants, such as dimeric surfactants, can stay clear for as long as a few days before precipitation occurs. Therefore precaution must be taken when working with these kinds of surfactants. Sometimes even though the solution looks homogeneous below the Krafft temperature, it is actually not at equilibrium. The size of the aggregates might be changing and vesicles might form.

To compare the different cooling times for different surfactants, conductivity was measured for three compounds, cetylpyridinium bromide (CPB), CTAB and 16-4-16 with temperature lowering down from high above T_k to lower than T_k . The results are shown



Figure 2.3.1-1 Conductivity of (a) CPB, (b) CTAB, and (c) 16-4-16 2Br- with temperature changing from high to low.

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in Figure 2.3.1-1. All three sets of measurements were finished within seven hours. Precipitates were observed for the two single chain surfactants CPB and CTAB, but not for the dimeric surfactant 16-4-16. The difference in their cooling times was also reflected in the conductivity values shown in the plots. A big drop in conductivity occurred for CPB at 23°C, which is 3 degrees lower than the Krafft temperature 26°C, and for CTAB at 17 °C, which is 7 degrees lower than its T_k , 24 °C. The conductivity of 16-4-16, however, never had a big drop during the whole measurement, not even at 15 °C, which is actually far lower than its Krafft temperature, 34 °C, which will be shown in Table 2.3-1. To avoid this long cooling time during the Krafft temperature measurement, the samples were forced to precipitate at or even lower than 0 °C, then the temperature was increased gradually until all precipitates dissolved.

2.3.1.2 Concentrations. It is normally considered that the Krafft temperature of a surfactant is independent of its concentration as long as the solution is above the cmc. In order to find out an appropriate concentration for making an accurate measurement, two sets of samples of 16-4-16 and CPB were made with three concentrations, 1.2 mM, 2.1 mM and 3.0 mM. The cmcs of these two compounds are both smaller than 1.2 mM, which will be shown in Table 2.3-1. The results of conductivity measurements are shown in Figure 2.3.1-2 and 2.3.1-3. Figure 2.3.1-2 shows that the breaks of all three CPB samples are at 26 °C, and Figure 2.3.1-3 shows that for all three 16-4-16 samples there are two breaks at 31.0 and 34.0 °C, respectively. According to the definition, the break for CPB at 26 °C or the break for 16-4-16 at higher temperature (34 °C) is referred to as the Krafft temperature. Since the break for 16-4-16 at lower temperature also falls in with the definition of the Krafft temperature by being independent of concentration, it will be called the "second Krafft temperature", or "Krafft temperature (II)" in the later discussion. Even though the same Krafft temperatures were obtained for all three concentrations, 3.0 mM



Figure 2.3.1-2 Conductivity of CPB with concentration of (a) 1.2 mM (b) 2.1 mM (c) 3.0 mM versus temperature.

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Figure 2.3.1-3 Conductivity of 16-4-16 2Br- with concentration of (a) 1.2 mM (b) 2.1 mM (c) 3.0 mM versus temperature.

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was chosen to be the concentration for the conductivity measurements for the rest of the pure dimeric surfactants and mixed surfactants. This is due to the better sensitivity of the more concentrated samples, which is especially important for the samples which have breaks at low temperature.

2.3.1.3 Krafft temperatures of m-s-m. 3 mM samples of all five dimeric surfactants, 16-6-16, 16-4-16, 16-2-16, 14-2-14 and 12-2-12 were made and the Krafft temperatures of m-s-m series were determined through electrical conductivity measurements in this work. The observed Krafft temperature T_k and T_k (II) are listed in Table 2.3-1 and the conductivity plots are shown in Figure 2.3.1-4. In order to make the comparison between dimeric surfactants and one chain surfactant, the monomer of 16-2-16, cetyltrimethylammonium bromide (CTAB) was also measured and the results of which are listed together with those of dimeric surfactants.

Figure 2.3.1-4 illustrates that the plots of conductivity against temperature only show one sharp break for CTAB and 12-2-12 and two breaks for all other m-s-m, which correspond to the Krafft temperature and Krafft temperature (II). Therefore for CTAB and 12-2-12, at temperatures far lower than the Krafft point, the solubility of the surfactant increases slowly with the increase of temperature. When the temperature is close to the Krafft temperature, the conductivity of the surfactant increases dramatically until it finally levels off after the Krafft point. Three of the other four dimeric surfactants, 14-2-14, 16-4-16, 16-6-16, have two breaks.



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Figure 2.3.1-4 Conductivity of (a) CTAB (b) 12-2-12 2Br⁻ (c) 14-2-14 2Br⁻ versus temperature.

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Figure 2.3.1-4 Conductivity of (d) 16-2-16 2Br⁻ (e) 16-4-16 2Br⁻ (f) 16-6-16 2Br⁻ versus temperature.

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Surfactant	т _к ', °С	T _k , ℃*	cmc, mM**
СТАВ	-	24.0	1.15
12-2-12	-	14.4	1.38
14-2-14	25.0	32.8	0.20
16-2-16	-	45.0	0.034
16-4-16	31.0	34.0	0.044
16-6-16	32.0	41.0	0.047

Table 2.3-1 Krafft Temperature T_k , T_k (II) and the cmc's of pure surfactants by Conductivity Measurements

* Krafft temperatures were determined with 3 mM samples

** The cmc's were determined at 46.5 °C; the details are discussed in Chapter 3.

It is difficult to interpret the second break at lower temperature just from conductivity data. However, based on some of the studies by Zana and co-workers [5, 9-10], we suggest that it may be related to the various conformations of the dimeric surfactants. They investigated the microstructures of two series of dimeric surfactants, 12-s-12 and 16-s-16, with cryogenic temperature transmission electron microscopy (Cryo-TEM) [5, 9-10] at room temperature. Their work demonstrated the diversity of microstructures for the dimeric surfactants. For example, thread-like micelles were observed for 20 mM 12-2-12 solution and 110 mM 12-3-12 solution, while only densely packed spherical or spheroidal micelles were observed for a 30 mM 12-3-12, a 78 mM 12-4-12, and a 71 mM 12-8-12 solution. The micrographs of a 138 mM 12-10-12 solution and of 66 and 133 mM solutions of 12-

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12-12 also show spherical or spheroidal micelles. A variety of microstructures, such as open membranes, thread-like and spheroidal micelles, were also observed for 16-s-16 series. Unfortunately, only the results of 12-s-12 homologues with small spacers are trustable, because the Krafft temperatures of 12-s-12 series with small s are lower than room temperature while the T_k of other series are all above room temperature. When Zana and his co-workers did the experiments, they didn't determine the Krafft temperatures first before they performed all other experiments at 25 °C. According to our experience, as long as the dimeric surfactant with high Krafft temperature is dissolved in water by heating, the solution won't precipitate until a few days later upon standing at room temperature. But it does not mean that the solution is homogeneous and in equilibrium. The way that Zana's group prepared samples was to clarify the samples by heating the water-surfactant mixture at 50 °C and then cool down to room temperature, where they stood for about 1 h before vitrification from 25 °C. As shown in Table 2.3-1, the Krafft temperatures of 16-s-16 with s value of 2, 4 and 6 are all above room temperature, and even though the Krafft temperatures of 12-s-12 with big s were not determined in our work, it is very possible that they are not soluble at room temperature either. During the time the samples stood, the aggregates in the solution became bigger and bigger to turn the solution cloudy and then precipitate eventually. Therefore, the Cryo-TEM results from Zana's group cannot reflect the real microstructures of dimeric surfactants in solution, because they are not at equilibrium. If those samples with high Krafft temperatures stood at room temperature for a longer time, the microstructures shown in the electron micrographs might be different.

Even though the electron micrographs of some of the dimeric surfactants obtained by Zana's group may not reflect the real microstructures in the condition which they claimed to be, it can still suggest that various conformations exist in dimeric solutions. The second break, or the second Krafft temperature, observed in the conductivity plots of some dimeric surfactants may be related to the various conformations in the solution.

2.3.2. Krafft temperature for mixed surfactant systems

As discussed in the earlier section, the Krafft temperature is such an important property of a surfactant that it has to be determined before studying other properties. However, in real application, it is very rare that a pure surfactant is used directly. There are always two or more surfactants mixed together in order to give a synergistic effect. Therefore, it is more meaningful in application to study a surfactant mixture than a pure surfactant. Similar as the study for pure surfactants, it is also important to determine the Krafft temperatures for a mixed surfactant system before other properties are further studied.

<u>2.3.2.1</u> SDS+SOBS system. A system of sodium dodecyl sulfate (SDS) and sodium octyl benzene sulfonate (SOBS) was studied by Scamehorn's group through visual observation [19]. The Krafft temperature curve is shown in Figure 2.3.2-2. Since the Krafft temperature of this system has not been studied systematically by conductivity measurement before, it is necessary to make a comparison between the conductivity method employed in this study and the one commonly used, the visual observation.

To compare the results obtained by the two methods, SDS and SOBS were purified the same way, and the concentrations of the samples were also the same as theirs, i.e., 0.04 M. The conductivity plots are shown in Figure 2.3.2-1 and the Krafft temperature plot is shown in Figure 2.3.2-2. Only one break was obtained for all samples in the conductivity plots except the sample with a SDS fraction of 0.4. Even though an eutectic curve was obtained which was similar to that obtained by Scamehorn's group, the Krafft temperature



Figure 2.3.2-1 Conductivity of the binary system SDS+SOBS versus the temperature with the mole fraction of SDS (a) 0, (b) 0.1, (c) 0.2, and (d) 0.3.

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Figure 2.3.2-1 Conductivity of the binary system SDS+SOBS versus the temperature with the mole fraction of SDS (e) 0.4, (f) 0.5, (g) 0.6, and (h) 0.7.











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Figure 2.3.2-2 Krafft temperature of the binary system "SDS+SOBS" versus the mole fraction of SDS.

values from our work are lower than those obtained by visual observation. This difference is caused from the more accurate conductance reading. The conductance reading would keep changing before the solution reached equilibrium, and in our experiments the temperature was not raised until the conductance reading was stabilized. On the other hand, in visual observation, sometimes the temperature might be raised before the solution has reached equilibrium, so that the Krafft temperature determined might be higher than its real value. Another advantage of the conductivity method is that the second, even the third Krafft temperature can be determined as shown in the phase diagrams for CTAB+m-s-m systems to be discussed below, while visual observation can only determine the first Krafft temperature. Even though the quantitative results of the two methods are different, the qualitative aspects and the "eutectic" composition are similar. Therefore, we are confident that the determination of the Krafft temperature by the use of conductivity is a viable one, and gives better quantitative results than the visual method.

2.3.2.2 CTAB+m-s-m system. Five CTAB+m-s-m systems were studied by conductivity measurements in this work. 10 mL, 3 mM samples were made for all five mixed surfactant systems. All samples were supercooled in ice-water or in a freezer at -18 °C to precipitate. Those precipitated in a freezer were then warmed up in the cold room at 4 °C. During the conductivity measurement, the temperature was raised gradually from low to high until all precipitates dissolved. Normally four or five readings were taken after the solution was clear. The plots of conductivities vs. temperatures are shown in Figure 2.3.2-3 to Figure 2.3.2-6. The temperatures where breaks occurred were assigned Krafft temperatures, second Krafft temperatures and third Krafft temperatures, which were plotted against the CTAB fractions in the solutions shown in Figure 2.3.2-8. The conductivity data for all five mixed CTAB+m-s-m systems and SDS+SOBS system are compiled in the Appendix

2A(a) to 2A(e) at the end of this chapter.

2.3.2.2.1 CTAB+12-2-12. From the conductivity plots shown in Figure 2.3.2-3, it can be seen that only one break was obtained for fractions of CTAB at 0, 0.1, 0.2, 0.3, 0.8, 0.9 and 1.0, while two breaks were obtained for fractions 0.4, 0.5, 0.6 and 0.7. The plot of the Krafft temperature against the mole fraction of CTAB is shown in Figure 2.3.2-8 (a). For mole fractions of CTAB in the range of 0 - 0.3 and 0.8 - 1.0, only one curve was obtained from Krafft temperature data. When the mole fraction of CTAB increased from 0.4 to 0.7, two Krafft temperatures were obtained. Therefore, two branches instead of one curve was obtained in the this range, which divided the phase diagram into three regions. Obviously, region I is the precipitation region, and region III contains a micelle solution. The Cryo-TEM results of Zana and co-workers may be helpful for understanding region II, which has never be seen in the T_k graph before. According to their electron micrographs at room temperature, long, thread-like and entangled micelles were seen in freeze-fractured aqueous solution of 12-2-12. When its monomer dodecyltrimethylammonium bromide (DTAB) was added to the 12-2-12 solution with the mole fraction increasing from 0.065 to 0.14 and then to 0.30, the electron micrographs showed the progressive disappearance of the thread-like micelles and appearance of spheroidal micelles [5]. Therefore it can be speculated that when CTAB was added to 12-2-12, the conformations of the micelles were also changed. In the system DTAB+12-2-12, since DTAB has the same chain length as 12-2-12, the size of the micelles became smaller when DTAB was added to 12-2-12. In the system CTAB+12-2-12, however, the chain length of CTAB is four carbons longer than that of 12-2-12 and the T_k of CTAB is 10 degrees higher than that of 12-2-12. When small fractions of 12-2-12 were mixed with CTAB, instead of decreasing, the Krafft temperature of 12-2-12 increased slightly, which probably indicates that larger size of micelles were



Figure 2.3.2-3 Conductivity of binary systems "CTAB+12-2-12 2Br-" versus temperature with mole fraction of CTAB (a) 0.1 (b) 0.2 (c) 0.3.

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Figure 2.3.2-3 Conductivity of binary systems "CTAB+12-2-12 2Br-" versus temperature with mole fraction of CTAB (d) 0.4 (e) 0.5 (f) 0.6.



Figure 2.3.2-3 Conductivity of binary systems "CTAB+12-2-12 2Br-" versus the temperature with mole fraction of CTAB (g) 0.7 (h) 0.8 (i) 0.9.

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formed. Therefore, it is possible that in the mixed surfactant system CTAB+12-2-12, more than one kind of micelles existed. When the precipitates in region I were heated, some precipitates started to dissolve first to form two kinds of micelles until the temperature reached the second Krafft temperature. When the temperature was raised further, a true equilibrium is reached, and the two kinds of micelles merge to form a single type of micelles.

2.3.2.2.2 CTAB+14-2-14. The conductivity versus temperature plots of CTAB+14-2-14 are shown in Figure 2.3.2-4. The plots of this system are more complicated than those of CTAB+12-2-12. Unlike 12-2-12, pure 14-2-14 (Fig. 2.3.1-4c) has two breaks as well as most of the CTAB+14-2-14 mixtures. Therefore the plot of the Krafft temperature versus the fraction of CTAB, or we may just simply call it a phase diagram, as shown in Figure 2.3.2-8 (b), is divided into four regions. In region I, only precipitates exist in equilibrium with surfactant monomers in solution. Region IV is a homogeneous micelle solution. Region II and III are the mixtures of precipitates and micelle solutions. It is difficult to speculate about the size and shape of the micelles in regions II and III only from conductivity data. However, the Small-Angle Neutron Scattering (SANS) studies of mixed CTAB+16-m-16 systems by De and co-workers [24] may be helpful in understanding of the system. Their results showed that the increase in temperature promotes a greater degree of ionization and thus in turn results in a decrease in the aggregation number, N. Therefore, we can speculate that when the temperature of system CTAB+14-2-14 was increased further from the second Krafft temperature, the precipitates in region II and III were dissolved gradually until a homogeneous micelle solution was obtained when the first Krafft temperature was reached. Since the micelle size and shape are also affected significantly by the temperature according to the SANS results by De et al., it is possible



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Figure 2.3.2-4 Electron micrograph of 14-2-14 2Br⁻ at 50 °C.



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Figure 2.3.2-5 Conductivity of binary systems "CTAB+14-2-14 2Br-" versus temperature with mole fraction of CTAB (a) 0.1 (b) 0.2 (c) 0.3.

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Figure 2.3.2-5 Conductivity of binary systems "CTAB+14-2-14 2Br-" versus temperature with mole fraction of CTAB (d) 0.4 (e) 0.5 (f) 0.6.

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Figure 2.3.2-5 Conductivity of binary systems "CTAB+14-2-14 2Br-" versus temperature with mole fraction of CTAB (g) 0.7 (h) 0.8 (i) 0.9.

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that the larger sized micelles in region II and III were broken into the smaller sized micelles in region IV. The size breaking with the increase of the temperature is also supported by the electron microscopy (EM) shown in Figure 2.3.2-4. As shown in the EM picture, the shape of the micelles at 50 °C is either elliptical or disk-like. As discussed earlier, the shape of the 12-2-12 micelles at room temperature is rod-like, it is therefore very possible that 14-2-14 is also rod-like. The shape of the 14-2-14 micelles in the EM picture, however, is ellipsoidal or disk-like, which means that the larger size of the 14-2-14 micelles might have been broken into smaller size at 50 °C.

<u>2.3.2.2.3 CTAB+16-2-16</u>. The T_k of 16-2-16 is higher than that of both 12-2-12 and 14-2-14. As a matter of fact, it is the highest among the Krafft temperatures of all five dimeric surfactants being studied in this work as will be shown in Table 2.3-1. From the conductivity plots shown in Figure 2.3.2-5, there is only one break for the pure 16-2-16 and the samples with smaller CTAB fractions. The second break is clearly shown in the conductivity plots of fractions 0.7, 0.8 and 0.9. The Krafft temperature plot illustrated in Figure 2.3.2-8 (c) doesn't show a good eutectic curve as those of 12-2-12 and 14-2-14 do. It can also be seen from the phase diagram that 16-2-16 hardly mixed with CTAB, because the Krafft temperature of 16-2-16 was only lowered slightly with the addition of CTAB.

Any physical properties can be related to the microstructures of the compound. The microstructures of the 16-s-16 series were obtained by Zana [9] for s = 3, 4, 6 and 8. Threadlike micelles, vesicles, and bilayer membrane fragments were observed in the micrograph of a 12 mM 16-3-16 solution. Entangled threadlike micelles and some open membranes and spheroidal micelles are seen in a 45 mM 16-4-16 solution. However, a 51 mM solution of 16-6-16 showed only spherical or slightly elongated micelles. Even



Figure 2.3.2-6 Conductivity of binary systems "CTAB+16-2-16 2Br-" versus the temperature with mole fraction of CTAB (a) 0.1 (b) 0.2 (c) 0.3.

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Figure 2.3.2-6 Conductivity of binary systems "CTAB+16-2-16 2Br-" versus temperature with mole fraction of CTAB (d) 0.4 (e) 0.5 (f) 0.6.

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Figure 2.3.2-6 Conductivity of binary systems "CTAB+16-2-16 2Br-" versus temperature with mole fraction of CTAB (g) 0.7 (h) 0.8 (i) 0.9.

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though the micrograph of 16-2-16 was not obtained with no reason given, it can be speculated from the microstructures of its homologues that thread-like micelles may be formed in 16-2-16 solution due to its even shorter spacer than 16-3-16. It can be seen that in the mixed CTAB+16-2-16 system, 16-2-16 controls the morphology of the mixed micelles in almost the whole range of proportions. Even though the T_k of the mixture decreases slightly with the adding of CTAB, the second break doesn't occur until the fraction of CTAB increases to 0.7.

As discussed in the introduction, micellization and precipitation are two competitive processes in a surfactant solution. One way to decrease the precipitation, or to lower the Krafft temperature, is to increase the micellization. Figure 2.3.3-8 (c) shows that the Krafft temperature of 16-2-16 only decreases slightly while CTAB was added to the solution of 16-2-16, which means that the co-micellization of 16-2-16 and CTAB is not significant which may be due to the compact aggregation of 16-2-16. Therefore, due to its high Krafft temperature and difficult mixing property, 16-2-16 may not have much applicable value as far as detergency is concerned.

<u>2.3.2.2.4</u> CTAB+16-4-16. As discussed in an earlier section, the spacer affects the properties of dimeric surfactant significantly. Therefore, another m-s-m with a longer spacer, 16-4-16, was studied in this work to compare their properties with that of 16-2-16. As shown in the conductivity plots in Figure 2.3.2-6, most of the fractions except 0.9 have two breaks. The Krafft temperature plot is shown in Figure 2.3.2-8 (d).

As discussed in section 2.3.2.2.3, Zana's electron micrographs showed that entangled threadlike micelles and some open membranes and spheroidal micelles were obtained from



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Figure 2.3.2-7 Conductivity of binary systems "CTAB+16-4-16 2Br-" versus temperature with mole fraction of CTAB (a) 0.1 (b) 0.2 (c) 0.3.

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Figure 2.3.2-7 Conductivity of binary systems "CTAB+16-4-16 2Br-" versus temperature with mole fraction of CTAB (d) 0.4 (e) 0.5 (f) 0.6.

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Figure 2.3.2-7 Conductivity of binary systems "CTAB+16-4-16 2Br-" versus temperature with mole fraction of CTAB (g) 0.7 (h) 0.8 (i) 0.9.

a 45 mM 16-4-16 solution. Even though the concentration of the sample for the Krafft temperature measurement in this work was only 3 mM, it is still possible that different kinds of micelles co-exist in the solution. When CTAB was added to the solution of 16-4-16, two or more kinds of mixed micelles may form. This may explain the Krafft temperature curve at higher temperature and the eutective curve at lower temperature in the phase diagram of 16-4-16+CTAB in Figure 2.3.3-8 (d). One significant difference between this system and system CTAB+16-2-16 is that Krafft temperature at 34 °C for pure 16-4-16 is constant for mole fraction of CTAB from 0 to 0.2. However, with the adding of CTAB, the T_k at 34 °C dissapeared at the CTAB fraction 0.2, which indicates that the aggregates formed by 16-4-16 are not as compact as those formed by 16-2-16 so that the large aggregates was broken down easily with the addition of CTAB.

2.3.2.2.5 <u>CTAB+16-6-16</u>. The conductivity plots and Krafft temperature plot of CTAB+16-6-16 system in Figure 2.3.2-7 and Figure 2.3.2-8 (e) are similar to those of CTAB+16-4-16 except that the Krafft temperatures of the later are lower in general. In the system of CTAB+16-4-16, the first Krafft temperature curve only lasts until CTAB fraction 0.2, while in the CTAB+16-6-16 system, it lasts until CTAB fraction 0.5. In system of CTAB+16-4-16, the eutectic curve, or we may call it the third Krafft temperature curve, starts at fraction 0.2 and ends at fraction 0.8, while in system of CTAB+16-6-16, a eutectic curve was not observed at all. If the system CTAB+16-6-16 is compared with that of 16-2-16, it can be seen that the effect of the spacers on the dimeric surfactants is very complicated. A spacer as short as 2 makes the two alkyl chains tightly bind together so that other single chains can hardly penetrate into the aggregates and the Krafft temperature can only be lowered slightly. A longer spacer, for example 4, may lower the Krafft temperature by making less compact aggregates. If the spacer is made even longer, such as



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Figure 2.3.2-8 Conductivity of binary systems "CTAB+16-6-16 2Br-" versus temperature with mole fraction of CTAB (a) 0.1 (b) 0.2 (c) 0.3.

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Figure 2.3.2-8 Conductivity of binary systems "CTAB+16-6-16 2Br-" versus temperature with mole fraction of CTAB (d) 0.4 (e) 0.5 (f) 0.6.

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Figure 2.3.2-8 Conductivity of binary systems "CTAB+16-6-16 2Br-" versus temperature with mole fraction of CTAB (g) 0.7 (h) 0.8 (i) 0.9.

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Figure 2.3.2-9 Krafft temperature of binary systems "CTAB+m-s-m 2Br-" versus the mole fraction of CTAB for (a) 12-2-12; (b) 14-2-14.

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Figure 2.3.2-9 Krafft temperature of binary systems "CTAB+m-s-m 2Br-" versus the mole fraction of CTAB for (d) 16-2-16; (e) 16-4-16; (f) 16-6-16.

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6 carbons, it will curve back inside the aggregates and make the conformation compact again. This result seems contradictory with the micrographs of cryo-TEM by Zana [9]. Their micrographs of a 51 mM solution of 16-6-16 showed only spherical or slightly elongated micelles while entangled threadlike micelles were seen in the micrographs of 16-4-16 solution. According to their micrographs, less compact aggregates were formed in the solution of 16-6-16. However, as discussed in the earlier sections, the experimental results obtained by Zana and co-workers were not reliable because they were not obtained at equilibrium conditions. Therefore, no conclusions should be drawn at this time. Since the study of conductivity does not reflect the microstructures of the dimeric surfactants, further study is necessary for getting more information about the dimeric surfactants.

Even though the study in this work is not sufficient yet for getting the information about the microstructures of dimeric surfactants, it can still be summarized that a sixteen carbon alkyl chain is too long to make the dimeric surfactants for practical applications at room temperature.

2.3.2.3 Conclusions. It has been shown that the conductivity method is a more accurate and informative method than visual observation in the determination of the Krafft temperature. From the study of systems CTAB+m-s-m, Krafft temperature phase diagrams were obtained, which include two or three Krafft temperature curves while normal visual observation could only determine the first one. The results show that the Krafft temperatures of m-s-m are strongly dependent on their microstructures. The longer the alkyl chain, the higher the Krafft temperature. For a short spacer, for example 2, the T_k increases from 14.4 °C to 45.0 °C when the alkyl chain length changes from 12 to 16 carbons. For a certain alkyl chain length, the effect of the spacer on the Krafft temperature is more complicated. In the case of sixteen carbon chain length, T_k changes from 45.0 to 34.0 and 40.0 °C for the spacer length of 2, 4 and 6 carbons. From conductivity data, it is difficult to explain how the spacers affect the the microstructures. However, it is possible that compact conformations are formed by the too short or too long spacers so that a lower energy state can be maintained.

In a surfactant solution, micellization and precipitation are two competitive processes. One way to reduce precipitation is to increase the extent of micellization. Adding one surfactant to another surfactant system is a commonly used method to increase the micellization and lower the Krafft temperature. Through the study for five CTAB+m-s-m mixed surfactant systems as shown in Figure 2.3.3-8, a conclusion can be drawn that the dimeric surfactants with alkyl chain as long as 16 are not very valuable for real applications because their Krafft temperature cannot be lowered to room temperature even by adding another single chain surfactant. This conclusion is also supported by the SANS study by De and coworkers [24]. Their studies show that even though the adding of CTAB in the mixed micelles with 16-m-16 change the overall shape of the resulting aggregates into predominantly spherical microstructures, the dimeric surfactants 16-m-16 control the morphology. Their results also suggest that the mixed micellar growth in the CTAB+16m-16 system depends on the concentrations of the dimeric surfactant and the length of their spacers. Our work, as well as Zana and De's study, however, all show that the dimeric surfactants with shorter chains, for example 14 and 12, have a better tendency to mix with the single chain surfactant CTAB, and therefore, a synergistic effect can be expected to occur.

Bibliography

- 1. F. Devinsky, L. Massarova, I. Lacko, J. Colloid Interface Sci. 1985, 105, 235.
- 2. R. Zana, M. Benrraou, and R. Rueff, Langmuir 1991, 7, 1072-1075.
- 3. E. Alami, H. Levy, and R. Zana, Langmuir 1993, 9, 940-944.
- 4. R. Zana, and Y. Talmon, Nature 1993, 362, 228.
- 5. E. Alami, G. Beinert, P. marie, and R. Zana, Langmuir 1993, 9, 1465-1467.
- 6. M. Frindi, B. Michels, H. Levy and R. Zana, Langmuir 1994, 10, 1140.
- 7. F. Kern, F. Lequeux, R. Zana, and S. J. Candau, Langmuir 1994, 10, 1714.
- D. Danino, A. Kaplun, Y. Talmon, and R. Zana, Cryo-Transmission Electron Microscopy Investigations of Unusual Amphiphilic Systems in Relation to Their Rheological Properties in "Structure and Flow in Surfactant Solutions", ACS symposium series 578, C. A. Herb and R. K. Prud'homme, Ed., 1994.
- 9. D. Danino, Y. Talmon, and R. Zana, Langmuir, 1995, 11, 1448-1456.
- 10. R. Zana and H. Levy, Langmuir 1997, 13, 402-408.
- 11. K. Esumi, K. Taguma, and Y. Koide, Langmuir 1996, 12, 4039-4041.
- 12. B. R-Roszak, E. Fisicaro, and A. Ghiozzi, J. Colloid Interface Sci. 1996, 184, 209-215.
- 13. M. J. Rosen, Chemtech 1993, 30.
- 14. J. Israelachvili, D. J. Mitchell., and B. Ninham, J. Chem. Soc., Faraday Trans. 2 1976, 72, 1525.
- 15. C. Tanford, J. Phys. Chem. 1972, 76, 3020.
- 16. J. F. Scamehorn, Precipitation of Mixtures of Anionic Surfactants in "Mixed Surfactant Systems", ACS Symposium 501, Ed. P. M. Holland and D. N. Rubingh, 1992.

- 17. J. F. Scamehorn and J. H. Harwell, *Precipitation of Surfactant Mixtures* in "Mixed Surfactant Systems", Ed. K. Ogino and M. Abe, Marcel Dekker, New York, 1993, Chapter 10.
- 18. K. L. Stellner and J. F. Scamehorn, Langmuir 1989, 5, 70

- 19. C. H. Rodriguez, J. F. Scamehorn, World Surfactants Congr., 4th, 1996, 2, 188-200.
- 20. K. L. Stellner and J. F. Scamehorn, J. Am. Oil Chem. Soc. 1986, 63, 566.
- 21. J. M. Peacock and E. Matijevic, J. Colloid Interface Sci. 1980, 77, 548.
- 22. J. F. Scamehorn, Ph. D. Dissertation, University of Texas, 1980.
- 23. K. Ogino, K. Kato, and M. Abe, J. Am. Oil Chem. Soc. 1988, 65, 272.
- 24. S. De, V. K. Aswal, P. S. Goyal, and S. Bhattacharyl, J. Phys. Chem. B 1997, 101, 5639-5645.

Appendix

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Table 2A Krafft Temperature of CTAB

Т, °С	κ, mS/cm	T, ℃	κ, mS/cm
3.0	0.48	34.9	1.62
8.8	0.59	37.8	1.67
11.7	0.66		
14.0	0.71		
17.0	0.82		
19.2	0.92		
20.0	0.94		
21.0	1.01		
22.2	1.10		
23.2	1.32		
23.9	1.47		
24.2	1.48		
25.0	1.51		
25.7	1.52		
26.0	1.53		
26.8	1.54		
27.9	1.55		
30.0	1.57		
32.8	1.61		

y(CTAB) = 0		y (CTAB) = 0.1	
T, ℃	κ, mS/cm	Т, °С	κ, mS/cm
			• • •
3.2	3.29	0.0	3.13
4.3	3.30	1.1	3.17
5.3	3.34	2.0	3.17
6.3	3.39	3.0	3.19
7.1	3.42	4.0	3.23
8.2	3.47	5.0	3.26
9.0	3.51	6.0	3.29
10.0	3.55	6.9	3.32
11.1	3.63	8.0	3.35
12.1	3.73	8.8	3.41
13.1	3.86	9.1	3.42
14.3	4.03	10.2	3.54
15.3	4.07	11.2	3.64
16.1	4.07	12.0	3.74
17.0	4.08	13.0	3.86
17.8	4.10	14.0	3.90
		15.2	3.91
		16.1	3.93
		17.6	3.94

Table 2A-(a) Krafft Temperature of Binary System CTAB+12-2-12 2Br⁻

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Table 2A-(a)	Krafft Temperature	of Binary System C	TAB+12-2-12 2Br ⁻

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y (CTAB) = 0.2		y (CTAB) = 0.3	
T, ° C	κ, mS/cm	T, ℃	κ, mS/cm
0.0	2.79	0.0	2.56
1.1	2.81	1.3	2.56
2.0	2.83	2.8	2.60
3.0	2.85	4.7	2.67
4.0	2.86	5.3	2.73
5.0	2.89	6.0	2.78
6.0	2.92	7.1	2.87
6.9	2.95	8.2	3.12
8.0	3.01	9.0	3.27
8.8	3.06	10.8	3.29
9.1	3.09	12.0	3.31
10.2	3.20	13.0	3.33
11.2	3.30	14.0	3.35
12.0	3.43		
13.0	3.58		
14.0	3.64		
15.2	3.65		
16.1	3.66		
17.6	3.68		
18.6	3.69		

Table 2A-(a) Krafft Temperature of Binary System CTAB+12-2-12 2Br	
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y (CTAB) = 0.4		y (CTAB) = 0.5		
T, ℃	к, mS/cm	T, ℃	κ, mS/cm	
1.1	2.38	1.0	2.09	
2.9	2.38	2.1	2.09	
5.0	2.44	3.5	2.09	
6.0	2.53	4.8	2.14	
7.1	2.65	5.3	2.19	
8.0	2.80	6.1	2.27	
8.9	2.95	7.0	2.34	
10.0	3.00	8.0	2.42	
10. 9	3.01	9.1	2.55	
11.9	3.03	10.1	2.65	
12.5	3.04	11.4	2.69	
13.1	3.05	12.9	2.70	
14.0	3.06	14.0	2.71	
15.0	3.07	15.0	2.72	
16.0	3.07	16.0	2.73	
16.9	3.07	16.9	2.74	
18.0	3.10	18.0	2.75	
19.0	3.11	18.9	2.77	
20.0	3.11	19.8	2.79	
21.0	3.11	21.0	2.82	

y (CTAB) = 0.4		y (CTAB) = 0.5	
T, ℃	κ, mS/cm	T, °C	κ, mS/cm
22.0	3.12	22.0	2.85
		23.0	2.87
		24.2	2.89
		25.4	2.89
		27.0	2.91
		29.0	2.95
		31.0	2.98

Table 2A-(a) Krafft Temperature of Binary System CTAB+12-2-12 2Br⁻

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Table 2A-(a) Kra	afft Temperature (of Binary S	System CTA	B+12-2-12 2H	Br ⁻
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y (CTAB) = 0.6		y (CTAB) = 0.7	
T, °C	κ, mS/cm	T, ℃	κ, mS/cm
3.0	2.01	3.2	1.71
4.0	2.01	4.0	1.76
5.0	2.05	5.0	1.85
6.0	2.10	5.8	1.90
7.0	2.16	6.3	1.94
8.0	2.24	7.1	1.99
9.0	2.30	8.0	2.05
10.0	2.35	9.0	2.08
10.9	2.38	10.0	2.09
11.8	2.39	10.9	2.10
12.4	2.40	11.6	2.10
13.3	2.41	12.7	2.10
14.2	2.42	13.8	2.11
15.1	2.42	16.2	2.13
16.0	2.43	19.0	2.14
16.8	2.43	21.9	2.16
18.0	2.46	22.3	2.17
19.0	2.46	23.1	2.18
19.9	2.47	24.0	2.20
20.8	2.48	25.0	2.32

Table 2A-(a) Krafft Temperature of Binary System CTAB+12-2-12 2Br⁻

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y (CTAB) = 0.6		y (CTA	B) = 0.7
T, ℃	κ, mS/cm	Т, °С	κ, mS/cm
22.0	2.50	26.0	2.36
23.0	2.52	27.0	2.37
24.0	2.55	28.1	2.39
25.1	2.60	29.2	2.41
26.1	2.65		
27.0	2.65		
28.0	2.66		
29.0	2.67		

Table 2A (a)	Knofft Tom	nometrume of	Dinam C	Swotom (CT & D . 13	2 12 2D
Table ZA-(a)	Manu Iem	perature or	Dulary 3	ystem (·2-12 2DC

y (CTAB) = 0.8		y (CTAB) = 0.9	
T, ℃	κ, mS/cm	T, ℃	κ, mS/cm
3.2	1.54	-4.0	0.96
4.0	1.55	-2.0	0.96
5.0	1.56	1.0	0.98
5.8	1.57	2.8	0.99
6.3	1.59	5.0	1.03
7.1	1.61	8.0	1.05
8.0	1.63	10.9	1.11
9.0	1.66	13.8	1.17
10.0	1.66	16.1	1.23
10.9	1.67	17.1	1.27
11.6	1.69	18.0	1.30
12.7	1.71	19.0	1.33
13.8	1.72	20.9	1.39
16.2	1.76	21.5	1.41
19.0	1.78	22.0	1.43
21.9	1.81	23.0	1.50
22.3	1.83	23.8	1.66
23.1	1.84	24.5	1.77
24.0	1.86	25.3	1.78
25.0	2.05	26.0	1.78

Table 2A-(a) Krafft Temperature of Binary System CTAB+12-2-12 2Br⁻

y (CTAB) = 0.8		y (CTAB) = 0.9	
Τ, ℃	κ, mS/cm	T, ℃	κ, mS/cm
26.0	2.06	27.2	1.80
27.0	2.08	29.1	1.83
28.1	2.09		
29.2	2.12		

Table 2A-(b)	Krafft Temperature	of Binary System	CTAB+14-2-14 2Br ⁻
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y(CTAB) = 0		y (CTAB) = 0.1	
Т, °С	κ, mS/cm	T, ℃	κ, mS/cm
8.0	2 77	1.8	2 4 1
11.0	2.77	6.2	2.71
11.0	2.77	0.2	2.44
13.0	2.77	9.2	2.47
16.0	2.80	12.0	2.51
19.0	2.82	14.9	2.52
21.9	2.84	17.2	2.53
24.0	2.86	20.0	2.54
25.0	2.87	23.0	2.60
25.9	2.87	23.9	2.67
26.3	2.87	24.5	2.72
27.0	2.87	25.1	2.68
27.9	2.87	26.0	2.65
28.7	2.88	27.1	2.65
29.3	2.89	28.0	2.65
30.1	2.92	29.0	2.71
31.0	2.97	29.9	2.80
31.9	3.04	30.9	2.96
32.2	3.13	31.3	3.20
33.0	3.33	32.0	3.52
34.0	3.33	32.8	3.67

Table 2A-(b) Krafft Temperature of Binary System CTAB+14-2-14 2Br⁻

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y (CTAB) = 0		y (CTAB) = 0.1	
T, ℃	κ, mS/cm	Τ, ℃	κ, mS/cm
35.0	3.33	33.8	3.68
36.0	3.33	35.0	3.69
37.0	3.34	36.0	3.71
		37.0	3.72
Table 2A-(b)	Krafft Temperature	of Binary System	CTAB+14-2-14 2Br
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y (CTAB) = 0.2		y (CTAB) = 0.3		
T, ℃	κ, mS/cm	Т, °С	κ, mS/cm	
5.0	2.41	2.0	2.09	
7.9	2.41	4.0	2.12	
10.5	2.44	6.9	2.12	
12.9	2.47	9.1	2.14	
14.0	2.48	12.1	2.23	
15.8	2.52	13.1	2.24	
16.9	2.57	14.1	2.25	
18.0	2.60	15.0	2.26	
19.0	2.64	16.0	2.27	
19.9	2.65	16.9	2.28	
21.0	2.66	17.8	2.33	
22.1	2.67	18.2	2.40	
23.0	2.67	19.1	2.41	
24.0	2.67	20.0	2.41	
25.0	2.67	21.1	2.42	
26.0	2.68	22.0	2.44	
26.9	2.69	22.8	2.47	
28.0	2.71	23.5	2.48	
29.0	2.74	24.1	2.49	
30.0	2.81	25.0	2.49	
30.4	2.85	26.1	2.53	

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y (CTAB) = 0.2		у (СТ	(AB) = 0.3
T, °C	κ, mS/cm	T, ℃	κ, mS/cm
30.9	2.85	27.0	2.57
32.0	2.85	27.9	2.60
33.0	2.86	28.8	2.62
34.0	2.86	29.2	2.62
		30.0	2.62
		31.0	2.63
		31.9	2.64

Table 2A-(b)	Krafft Temperature of	f Binary System	CTAB+14-2-14 2Br ⁻
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y (CTAB) = 0.4		y (CTAB) = 0.5		
T, ℃	κ, mS/cm	T, ℃	κ, mS/cm	
7.5	1.89	5.0	1.67	
9.0	1.93	7.0	1.69	
9.5	1.94	9.0	1.70	
10.0	1.94	11.0	1.70	
11.0	1.96	12.0	1.71	
12.0	1.97	13.0	1.73	
13.0	1.98	14.0	1.74	
15.0	2.00	15.0	1.82	
16.1	2.02	16.0	1.88	
16.9	2.05	17.0	2.01	
18.0	2.09	17.5	2.14	
18.5	2.20	18.0	2.19	
19.0	2.20	19.0	2.21	
20.1	2.20	20.0	2.22	
21.0	2.25	21.0	2.22	
22.0	2.30	22.0	2.23	
23.0	2.33	23.0	2.24	
24.0	2.35			
24.9	2.37			
26.0	2.39			

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y (CTAB) = 0.4		y (CTA	(AB) = 0.5
Γ, °C κ, mS/cm		T, ℃	κ, mS/cm
27.0	2.41		
28.0	2.41		
29.0	2.41		
30.0	2.42		
31.0	2.43		

y (CTAB) = 0.6		y (CTAB) = 0.7	
Т, °С	κ, mS/cm	T, ℃	κ, mS/cm
2.0	1.28	2.1	1.00
4.0	1.33	3.9	1.08
7.0	1.35	6.8	1.11
9.2	1.37	9.2	1.14
10.0	1.39	12.1	1.17
11.0	1.43	14.9	1.22
12.0	1.47	15.5	1.25
12.9	1.49	16.5	1.38
13.5	1.51	17.1	1.44
15.0	1.56	18.0	1.51
16.0	1.60	18.9	1.57
16.8	1.68	19.4	1.58
18.0	1.82	20.7	1.63
19.0	1.85	21.8	1.68
19.8	1.86	22.8	1.74
20.2	1.88	23.3	1.78
21.1	1.91	24.2	1.89
22.0	1.94	25.2	1.92
23.0	2.02	26.1	1.95
23.8	2.03	27.1	1.97

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y (CTAB) = 0.6		y (CTA	(B) = 0.7
T, ℃	κ, mS/cm	T, ℃	κ, mS/cm
24.8	2.04		
25.7	2.05		
27.0	2.07		

Table 2A-(b)	Krafft Temp	erature of	Binary Sy	ystem CT	`AB+14-2-14 2I	Br-
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y (CTAB) = 0.8		y (CTAB) = 0.9	
T, ℃	κ, mS/cm	T, ℃	κ, mS/cm
2.0	0.81	1.8	0.61
4.0	0.82	4.0	0.61
7.0	0.85	6.9	0.66
9.1	0.89	9.1	0.68
12.0	0.92	12.0	0.72
14.9	0.97	14.8	0.76
17.7	1.10	17.5	0.93
18.2	1.20	20.0	1.16
19.1	1.33	21.0	1.25
20.0	1.33	21.7	1.38
20.9	1.38	22.2	1.45
21.7	1.42	23.0	1.63
22.9	1.49	24.0	1.65
23.9	1.74	25.0	1.66
24.2	1.82	25.9	1.69
25.1	1.83	26.8	1.70
26.0	1.84	27.3	1.71
27.0	1.84	28.0	1.71
28.0	1.85		

y (CTAB) = 0		y (CTA	y (CTAB) = 0.1	
Τ, ℃	κ, mS/cm	Τ, ℃	κ, mS/cm	
18.2	5 51	18.0	4.97	
21.0	5.51	20.8	5.01	
23.0	5.51	24.0	5.02	
26.0	5.51	26.8	5.02	
28.2	5.51	29.0	5.02	
31.8	5.55	31.3	5.02	
34.0	5.57	34.1	5.03	
37.0	5.58	36.8	5.11	
39.0	5.60	38.0	5.14	
40.6	5.63	39.0	5.15	
42.0	5.71	39.9	5.17	
43.0	5.80	41.0	5.26	
44.0	5.86	42.0	5.35	
45.4	6.08	43.0	5.48	
46.0	6.10	43.8	5.77	
47.0	6.13	44.4	5.81	
48.2	6.14	45.1	5.83	
49.2	6.16	46.3	5.86	
50.2	6.16	48.8	5.92	
52.0	6.19			

Table 2A-(c)	Krafft Temperature	of Binary System	CTAB+16-2-16 2Br-
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.

y (CTAB) = 0.2		y (CTAB) = 0.3	
T, ℃	κ, mS/cm	T, ℃	κ, mS/cm
16.0	4.19	14.2	4.37
17.9	4.20	16.5	4.37
20.1	4.20	19.0	4.37
23.0	4.20	22.0	4.37
25.9	4.20	25.0	4.37
28.2	4.20	27.3	4.37
31.0	4.22	32.8	4.45
31.9	4.23	33.2	4.47
33.0	4.24	34.1	4.50
34.0	4.25	35	4.51
35.0	4.26	35.9	4.52
36.0	4.27	36.8	4.52
37.0	4.28	37.3	4.57
37.9	4.30	38.8	4.73
38.5	4.32	39.3	4.85
39.5	4.37	40.1	4.96
40.1	4.46	41.2	5.14
41.0	4.59	30.0	4.37
41.8	5.05	42.2	5.15
42.9	5.51	43.2	5.16

Table 2A-(c) Krafft Temperature of Binary System CTAB+16-2-16 2Br-

y (CTAB) = 0.2		y (CTAB) = 0.3	
Т, °С	κ, mS/cm	T, ℃	κ, mS/cm
43.3	5.51	44.0	5.17
44.0	5.51	46.0	5.19
45.1	5.55		
46.8	5.58		

Table 2A-(c)	Krafft Temperature of Binary System CTAB+16-2-16 2Br-	
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y (CTA	AB) = 0.4	y (CTA	(B) = 0.5
T, ℃	κ, mS/cm	T, ℃	κ, mS/cm
17.2	3.66	6.9	1.88
23.0	3.73	9.3	2.06
25.0	3.73	11.8	2.06
28.0	3.77	15.0	2.16
30.6	3.83	17.2	2.18
33.2	3.90	20.0	2.18
34.2	3.92	21.0	2.18
35.8	4.02	22.0	2.18
36.5	4.10	23.0	2.18
37.2	4.27	24.0	2.18
38.2	4.43	25.0	2.18
39.2	4.55	25.5	2.18
40.2	4.64	26.1	2.18
41.0	4.68	27.1	2.18
41.4	4.75	28.1	2.18
42.2	4.76	29.0	2.18
43.8	4.77	29.5	2.18
45.2	4.79	30.3	2.20
		31.2	2.23
		32.0	2.26
		32.9	2.30

y (CTAB) = 0.4		y (CTAB) = 0.5	
T, ℃	κ, mS/cm	T, ℃	κ, mS/cm
		33.5	2.39
		34.1	2.47
		35.0	2.57
		35.9	2.82
		36.6	3.13
		37.4	3.45
		38.1	3.76
		39.0	4.12
		40.0	4.29
		40.7	4.29
		41.5	4.29
		43.0	4.31

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Table 2A-(c)	Krafft Temperature	of Binary System	CTAB+16-2-16 2Br ⁻
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;

y (CTAB) = 0.6		y (CTAB) = 0.7	
T, ℃	κ, mS/cm	T, ℃	κ, mS/cm
6.5	2.18	6.9	1.68
9.8	2.20	9.2	1.76
12.0	2.20	12.0	1.80
14.8	2.20	14.7	1.80
17.1	2.20	15.9	1.80
20.0	2.20	17.0	1.80
21.0	2.20	18.2	1.80
22.0	2.20	19.6	1.80
23.0	2.20	20.2	1.80
24.0	2.21	21.2	1.80
24.7	2.22	22.7	1.83
25.3	2.23	23.3	1.86
26.0	2.24	24.1	2.00
27.0	2.25	25.0	2.05
28.0	2.27	26.0	2.08
28.9	2.32	27.0	2.14
29.3	2.33	28.0	2.19
30.1	2.37	28.9	2.24
31.1	2.39	29.5	2.29
32.0	2.43	30.2	2.35

Table 2A-(c)	:) Krafft Temperature of Binary System CTAB+16-2-16 2Br
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y (CTAB) = 0.6		y (CTAB) = 0.7	
Т, °С	κ, mS/cm	Т, °С	κ, mS/cm
32.9	2.47	31	2.43
34.0	2.53	32	2.53
34.9	2.74	32.5	2.59
35.2	2.89	33.7	2.66
36.0	3.17	34.1	2.71
37.0	3.64	35.1	2.76
37.9	3.80	36.2	2.94
39.0	3.86	37.1	3.16
40.4	3.88	37.9	3.36
41.0	3.89	38.8	3.36
41.9	3.90	40.0	3.37
42.9	3.91	41.2	3.39
		42.5	3.41

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Table 2A-(c)	Krafft Temperature of Bin	ary System CTAB+16-2-16 2Br ⁻
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y (CTAB) = 0.8		y (CTAB) = 0.9	
T, °C	κ, mS/cm	T, ℃	κ, mS/cm
6.9	0.97	7.7	0.88
9.5	1.06	9.2	0.95
11.0	1.14	11.0	1.00
14.6	1.14	14.2	1.00
15.0	1.10	14.2	1.07
15.9	1.17	17.0	1.14
16.6	1.17	18.1	1.17
17.2	1.17	19.1	1.25
18.1	1.20	20.0	1.28
19.0	1.20	21.0	1.30
20.0	1.21	22.0	1.33
21.0	1.23	23.0	1.39
22.0	1.25	24.0	1.61
23.0	1.26	24.5	2.07
24.0	1.54	26.0	2.20
25.0	1.82	27.0	2.23
25.8	1.83	28.0	2.25
26.4	1.84	28.9	2.27
27.0	1.86	29.8	2.30
28.0	1.88	30.8	2.33
28. 9	1.90	31.8	2.36

y (CTAB) = 0.8		y (CTAB) = 0.9	
T, ℃	κ, mS/cm	T, ℃	κ, mS/cm
29.2	1.94	32.8	2.38
30.2	2.01	33.8	2.39
31.2	2.08	34.2	2.41
32.0	2.13	35.0	2.42
33.0	2.18	36.0	2.44
34.0	2.26	37.0	2.51
35.0	2.31	38.0	2.55
36.0	2.43	38.9	2.59
36.9	2.65	40.0	2.62
37.9	2.81	41.0	2.63
38.2	2.82	42.0	2.66
40.0	2.85	43.0	2.68
41.4	2.90		
42.1	2.91		

Table 2A-(d)	Krafft Temperature	of Binary System	CTAB+16-4-16 2Br ⁻
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y (CT	(AB) = 0	y (CTA	(AB) = 0.1
T, ℃	κ, mS/cm	T, ℃	κ, mS/cm
٥ <u>٨</u>	0.22	2.0	0.25
0.0	0.23	2.0	0.55
10.0	0.24	4.0	0.37
12.0	0.24	7.0	0.38
14.0	0.24	10.0	0.39
16.0	0.25	12.5	0.41
18.0	0.25	15.2	0.43
20.0	0.26	17.8	0.44
22.0	0.27	20.2	0.45
24.0	0.27	21.0	0.46
26.0	0.29	22.0	0.47
28.0	0.39	22.8	0.48
30.0	0.69	23.8	0.50
31.0	0.88	24.2	0.51
32.0	0.92	25.2	0.51
33.0	0.94	26.0	0.51
34.0	1.05	26.8	0.52
35.0	1.06	27.8	0.53
36.0	1.07	28.8	0.58
37.0	1.07	29.9	0.65
38.0	1.08	30.4	0.72

y (CTAB) = 0		y (CTAB) = 0.1	
T, ℃	κ, mS/cm	T, ℃	κ, mS/cm
		31.2	0.76
		32.1	0.78
		33.0	0.94
		34.0	1.09
		34.8	1.10
		36.0	1.10
		37.0	1.11
		38.0	1.11

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y (CTA	AB) = 0.2	y (CTA	AB) = 0.3
T, ℃	к, mS/cm	Τ, ℃	κ, mS/cm
2.0	0.55	1 2	0.55
2.0 4 0	0.55	4.0	0.55
6.9	0.57	6.9	0.58
9.7	0.58	10.0	0.61
12.9	0.60	12.0	0.65
15.0	0.61	14.9	0.68
17.4	0.62	17.8	0.74
20.1	0.64	20.6	0.78
23.0	0.66	22.2	0.82
23.6	0.68	25.2	0.85
24.2	0.70	28.0	0.94
25.0	0.70	29.0	1.03
26.0	0.71	30.0	1.10
27.0	0.72	30.3	1.12
27.7	0.74	31.1	1.13
28.1	0.75	32.0	1.13
29.0	0.76	33.0	1.14
29.9	0.82	33.8	1.15
30.7	0.87		
31.2	0.97		

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y (CTAB) = 0.2		y (CTA	B) = 0.3
T, ℃	κ, mS/cm	T, ℃	κ, mS/cm
32.0	0.98		
32.8	0.99		
33.2	1.00		
34.0	1.04		
35.0	1.04		
35.8	1.04		
36.4	1.05		
37.0	1.05		
37.8	1.05		
39.0	1.06		

y (CTA	(AB) = 0.4	y (CTA	B) = 0.5
Т, ℃	κ, mS/cm	T , ℃	κ, mS/cm
2.0	0.54	4.0	0.57
4.2	0.55	7.0	0.61
7.0	0.57	9.9	0.65
9.8	0.64	12.2	0.73
12.2	0.71	15.0	0.87
15.1	0.80	16.3	0.94
17.6	0.87	17.0	0.96
20.2	0.95	18.1	0.98
22.7	1.00	19.0	0.98
23.8	1.00	19.9	1.00
24.3	1.00	21.0	1.01
25.2	1.01	23.0	1.05
26.1	1.03	25.2	1.17
28.0	1.10	26.9	1.27
29.0	1.16	28.0	1.34
30.0	1.20	28.5	1.37
31.0	1.21	29.2	1.41
32.6	1.23	30.4	1.44
33.2	1.25	31.8	1.47
34.0	1.26	33.0	1.49
		33.9	1.50

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Table 2A-(d) Krafft Tempe	rature of Binary System	CTAB+16-4-16 2Br-
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y (CT	AB) = 0.6	y (CTA	B) = 0.7
T, ℃	κ, mS/cm	Τ, ℃	κ, mS/cm
10.0	0.61	6.0	0.59
12.0	0.67	8.0	0.61
14.0	0.76	10.0	0.66
16.0	0.83	12.0	0.71
18.0	0.88	14.0	0.78
19.0	0.92	16.0	0.84
20.0	1.01	18.0	0.91
21.0	1.10	20.0	1.11
22.0	1.23	21.0	1.24
23.0	1.26	22.0	1.35
24.0	1.30	23.0	1.37
25.0	1.36	24.0	1.40
26.0	1.40	25.0	1.43
27.0	1.45	26.0	1.48
28.0	1.50	27.0	1.49
29.0	1.50	28.0	1.51
30.0	1.51	29.0	1.51
31.0	1.52	30.0	1.52
32.0	1.53	31.0	1.53

Table 2A-(d) Krafft Temperature of Binary System CTAB+16-4-1	6 2Br ⁻
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y (CT	AB) = 0.8	y (CTAI	3) = 0.9
T, ℃	κ, mS/cm	T, ℃	κ, mS/cm
2.0	0.45	5.0	0.46
4.0	0.45	7.0	0.49
6.8	0.48	9.0	0.51
9.8	0.54	11.0	0.53
12.2	0.62	13.0	0.59
15.0	0.70	15.0	0.63
17.7	0.81	17.0	0.70
20.5	1.00	19.0	0.78
21.5	1.14	20.0	0.85
22.2	1.31	21.0	0.93
23.1	1.37	22.0	1.01
24.0	1.40	23.0	1.16
24.9	1.41	24.0	1.45
25.2	1.45	25.0	1.60
26.0	1.47	26.0	1.614
27.5	1.49	27.0	1.61
28.1	1.50	28.0	1.63
29.1	1.50	29.0	1.64
29.8	1.51		

Table 2A-(e)	Krafft Temperature	of Binary System	CTAB+16-6-16 2Br ⁻
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у (С	TAB)=0	y (CTA)	B) = 0.1
T, ℃	κ, mS/cm	Τ, °C	κ, mS/cm
5.0	0.64	4.0	0.65
7.0	0.65	7.0	0.66
9.0	0.65	9.9	0.67
11.0	0.65	12.2	0.68
13.0	0.65	15.0	0.68
15.0	0.66	17.9	0.69
17.0	0.66	18.9	0.69
19.0	0.66	20.9	0.70
21.0	0.66	22.9	0.71
23.0	0.67	24.2	0.73
25.0	0.70	26.0	0.76
26.0	0.77	28.1	1.04
27.0	0.80	29.0	1.19
28.0	0.86	29.9	1.28
29.0	0.91	30.7	1.40
30.0	0.98	31.2	1.58
31.0	1.08	32.1	1.78
32.0	1.14	33.0	1.83
33.0	1.16	34.5	1.84
34.0	1.21	36.0	1.86

Table 2A-(e)	Krafft Temperature	of Binary System	CTAB+16-6-16 2Br
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:

y (CT	'AB) = 0	у (СТ	(AB) = 0.1
T, ℃	κ, mS/cm	T, ℃	κ, mS/cm
35.0	1.27	36.5	1.89
36.0	1.37	37.2	1.92
37.0	1.50	38.0	2.00
38.0	1.69	39.0	2.09
39.0	2.12	39.9	2.16
39.5	2.24	40.9	2.20
40.0	2.29	43.2	2.22
41.0	2.31	44.1	2.23
42.0	2.31	45.0	2.24
43.0	2.32	46.0	2.25
44.0	2.33		

y (CTAB) = 0.2		y (CTAB) = 0.3	
T, ℃	κ, mS/cm	T, ℃	κ, mS/cm
14.8	0.84	10.0	0.81
17.0	0.84	12.3	0.86
20.0	0.86	15.0	0.91
22.9	0.87	18.0	0.98
25.1	0.89	20.8	1.01
28.0	0.95	22.0	1.02
29.0	0.99	24.0	1.05
29.9	1.08	25.0	1.05
30.9	1.26	27.0	1.09
31.4	1.41	28.0	1.13
32.2	1.62	30.0	1.36
33.1	1.67	31.0	1.54

32.0

32.8

33.8

34.7

35.3

36.2

37.4

38.5

39.8

1.72

1.75

1.75

1.76

1.78

1.80

1.88

1.96

1.98

Table 2A-(e) Krafft Temperature of Binary System CTAB+16-6-16 2Br⁻

34.0

34.9

35.9

36.7

37.2

38.5

39.2

40.9

42.0

1.67

1.68

1.70

1.72

1.75

1.93

2.04

2.06

2.07

Table 2A-(e) Krafft Temperature of Binary System CTAB+16-6-16 2Br-

÷

y (CTAB) = 0.2		y (CTAB) = 0.3	
Τ, ℃	κ, mS/cm	T, ℃	κ, mS/cm
43.0	2.08	40.9	1.99
44.0	2.09	42.0	2.00
		44.0	2.02

Table 2A-(e) Krafft Temperature	of Binary System CTAB+16-6-16 2Br
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y (CTA	(AB) = 0.4	y (CTA	B) = 0.5
T, ℃	κ, mS/cm	Т, °С	κ, mS/cm
9.9	0.76	9.9	0.58
12.2	0.84	12.2	0.68
15.0	0.95	15.0	0.81
17.9	1.08	17.9	0.93
20.2	1.20	20.2	1.18
21.2	1.23	21.2	1.21
22.0	1.25	22.0	1.24
23.4	1.26	23.4	1.27
25.1	1.28	25.1	1.30
26.0	1.31	26.0	1.33
27.0	1.32	27.0	1.33
28.0	1.35	28.0	1.35
29.0	1.41	29.0	1.38
30.0	1.55	30.0	1.46
31.0	1.64	31.0	1.51
32.5	1.70	32.5	1.52
34.0	1.72	34.0	1.54
35.0	1.74	35.0	1.56
36.1	1.77	36.1	1.61
37.2	1.83	37.2	1.69

y (CTAB) = 0.4		y (CTAB) = 0.5	
T, ℃	κ, mS/cm	T, ℃	κ, mS/cm
38.2	1.93	38.2	1.76
39.8	1.95	39.8	1.77
41.0	1.96	41.0	1.79
42.0	1.98	42.0	1.81

y (CTAB) = 0.6		y (CTAB) = 0.7	
T, ℃	κ, mS/cm	T, ℃	κ, mS/cm
4.0	0.67	4.2	0.61
6.5	0.68	6.8	0.64
0.5	0.08	0.0	0.65
9.0	0.74	9.0	0.05
12.0	0.82	12.1	0.76
14.2	0.88	14.8	0.86
17.0	1.13	16.0	0.92
18.2	1.27	17.0	1.00
19.9	1.40	18.1	1.11
20.9	1.42	19.0	1.20
21.9	1.44	20.0	1.32
23.2	1.47	21.0	1.42
24.2	1.49	22.0	1.47
25.1	1.51	22.9	1.48
26.7	1.54	23.9	1.49
27.2	1.57	24.8	1.53
28.1	1.61	25.8	1.56
29.6	1.67	26.6	1.59
31.0	1.68	27.2	1.61
32.0	1.69	28.0	1.64
33.0	1.70	28.9	1.64

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Table 2A-(e) Krafft Temperature of Binary System CTAB+16-6-16 2Br-

:

y (CTAB) = 0.6		y (CTAB) = 0.7	
Т, °С	κ, mS/cm	T, ℃	κ, mS/cm
34.0	1.71	30.0	1.65
		31.0	1.66
		32.9	1.68

Table 2A-(e)	Krafft Temperature of Binary System CTAB+16-6-16 2Br-	
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y (CTAB) = 0.8		y (CTA	y (CTAB) = 0.9	
T, ℃	κ, mS/cm	T, ℃	κ, mS/cm	
9.0	0.60	9.0	0.60	
11.4	0.66	11.4	0.63	
14.1	0.77	14.1	0.74	
17.1	0.94	17.1	0.87	
20.2	1.28	20.2	1.14	
21.2	1.41	21.2	1.27	
22.2	1.52	22.2	1.45	
23.0	1.55	23.0	1.54	
23.9	1.55	23.9	1.55	
24.5	1.56	24.5	1.569	
25.0	1.58	25.0	1.58	
25.2	1.59	26.1	1.60	
27.1	1.60	27.1	1.61	
28.1	1.61	28.1	1.62	
29.0	1.62	29.0	1.63	
30.0	1.63			

y (CTAB) = 0		y (CTAB) = 0.1	
Τ, ℃	κ, mS/cm	Τ, ℃	κ, mS/cm
3.0	5.20	8.0	7.75
5.4	5.59	10.0	8.40
8.6	6.00	12.0	9.00
11.2	6.23	14.0	9.74
14.1	6.29	16.0	10.65
16.8	6.68	18.0	12.19
19.2	7.59	20.0	14.01
22.0	8.60	21.0	15.15
22.9	9.79	22.0	16.06
23.4	11.22	23.0	16.17
24.2	12.97	24.0	16.22
25.0	16.12	25.0	16.26
25.8	16.33	26.0	16.28
26.7	16.39		
28.0	16.50		
29.5	16.53		

Table 2A-(f) Krafft Temperature of Binary System SDS+SOBS

	Table 2A-(f)	Krafft Tem	perature of Binary	y Systen	n SDS+SOBS
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y (CTAB) = 0.2		y (CTA	y (CTAB) = 0.3		
T, ℃	κ, mS/cm	T, ℃	κ, mS/cm		
2.0	8.30	2.0	9.47		
4.0	8.47	4.0	9.94		
7.0	9.03	6.0	10.62		
9.9	9.89	8.0	11.21		
12.1	10.90	9.0	11.57		
15.0	12.46	10.0	12.05		
15.9	13.12	11.0	12.55		
17.0	13.80	12.0	13.08		
17.9	14.49	13.0	13.62		
18.8	15.25	14.0	14.41		
19.9	15.61	15.0	15.18		
20.5	15.66	16.0	15.20		
21.2	15.72	17.0	15.24		
23.0	15.79	18.0	15.32		
24.0	15.84	19.0	15.38		
		20.0	15.42		

y (CTAB) = 0.4		y (CTAB) = 0.5		
T, ℃	κ, mS/cm	Т, °С	κ, mS/cm	
1.2	8.46	0.0	8.75	
4.0	9.45	1.0	8.91	
7.0	11.37	2.0	9.18	
8.0	12.55	3.0	9.79	
8.9	12.83	4.0	10.85	
9.9	13.05	5.0	12.46	
10.9	13.51	5.5	13.15	
11.7	14.08	6.0	13.94	
12.1	14.12	6.5	14.02	
13.0	14.19	7.0	14.107	
14.0	14.25	8.0	14.23	
		9.0	14.31	
		10.0	14.40	

Table 2A-(f) Krafft Temperature of Binary System SDS+SOBS

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y (CTAB) = 0.6		y (CTAB) = 0.7		
T, ℃	κ, mS/cm	Т, °С	κ, mS/cm	
0.0	8.14	3.0	9.75	
2.0	8.63	4.0	10.07	
4.0	9.57	6.0	10.80	
5.0	10.60	7.8	11.64	
6.0	12.09	8.5	12.24	
6.5	12.87	9.0	12.97	
7.0	13.58	10.2	13.56	
7.5	13.73	11.2	13.57	
8.0	13.86	13.0	13.62	
8.5	13.94	14.1	13.67	
9.0	13.96			
10.0	14.00			
11.0	14.06			

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Table 2A-(f) Krafft Temperature of Binary System SDS+SOBS
y (CTAB) = 0.8		y (CTAB) = 0.9		
T, ℃	κ, mS/cm	T, ℃	κ, mS/cm	
4.0	8.34	2.0	4.83	
6.0	8.73	4.0	5.26	
8.0	10.01	6.0	5.57	
9.0	11.20	8.0	5.63	
10.0	12.69	10.0	7.59	
11.0	13.74	11.0	8.85	
11.5	13.75	12.0	10.53	
12.0	13.76	12.5	11.49	
13.0	13.80	13.0	12.60	
14.0	13.86	13.5	13.43	
		14.0	13.59	
		15.0	13.63	
		16.0	13.68	
		17.0	13.74	

Table 2A-(f) Krafft Temperature of Binary System SDS+SOBS

Table 2A-(f) Krafft Temperature of Binary System SDS+SOBS

y (CTAB) = 1.0				
Т, °С	κ, mS/cm			
4.0	3.16			
6.0	3.16			
8.0	3.27			
10.0	3.54			
12.0	4.28			
13.0	5.12			
13.5	6.49			
14.0	10.21			
14.5	13.05			
15.0	13.56			
16.0	13.58			
17.0	13.62			
18.0	13.66			

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Chapter 3

Mixtures of Monomeric and Dimeric Cationic Surfactants П. Study of critical micelle concentration (стс)

3.1 Theory

3.1.1 Mixed micellar solutions

Similar to pure surfactant solutions, solutions of mixed surfactants also exhibit a variety of interesting and useful properties. For example, the interfacial tension of a surface can be lowered due to the adsorption of surfactant molecules at solution interfaces. When its physical properties, such as surface tension and conductivity, are plotted against the concentration, a break point will also be obtained, which corresponds to the mixed critical micelle concentration (cmc). At the mixed cmc, surfactant molecules undergo cooperative self-association to form large surfactant aggregates (micelles) with the hydrophobic chains of the molecules residing in the interior of the aggregates and the hydrophilic head groups at the surface in contact with aqueous solution. In this process, both ideal and nonideal mixing contributions may occur. Since the hydrophobic effect which drives the overall process is not specific with respect to the surfactant "head" group, the formation of randomly mixed surfactant aggregates is usually favored. This can be viewed as leading to the "ideal" component of mixing in the aggregate. In the case of mixtures with two types of different surfactants, non-ideal mixing may occur. The difference may be due to the nature of the head groups, such as that schematically illustrated in Figure 3.1.1-1 [1], where a mixture of two types of surfactant is indicated by open and filled circles

representing the head groups. The difference can also be due to the nature of the hydrophobic moities, such as hydrocarbon and fluorocarbon chains [2, 3]. This work is only concerned with the first type of non-ideal mixed surfactants.



Figure 3.1.1-1 Schematic representation of phenomena in a mixed micellar solution of two surfactant types, illustrated by open and filled head groups. Shown are representations of surfactant monomers, a mixed micelle, mixed monolayer at the air/solution interface, and a mixed bilayer aggregate at the (hydrophilic) solid-solution interface [1].

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3.1.2 Modeling of the mixed surfactant systems

In a mixed surfactant system of the first type, the mixing of the hydrophobic core is viewed as the "ideal" process and the electrostatic interactions between "head" groups can be viewed as the "nonideal" process. To help understand the complicated mixing process, some models were designed to treat the mixed micellization with various approaches. Approaches to modeling mixed surfactant systems can vary from simple thermodynamic treatments, which address only a few basic properties of the system, to more complex molecular models, which deal with properties such as micelle size and the composition distribution of mixed micellar aggregates. The well known models include the pseudophase separation model [4], mass action model [5-7], and molecular model [8-11]. Among these, the pseudophase model is the most widely used, and is also employed in this work. One basic, simplified assumption of the pseudophase model is that the monomers in the solution and the mixed micelles or other mixed surfactant aggregates can be treated like two separate phases [1, 12-14]. Results from the mass-action approach, which explicitly takes the number of molecules in the aggregates into account, show that the psudophase model is a good approximation for micelle sizes of about 50 or more molecules [6, 15].

<u>3.1.2.1</u> Pseudophase modeling of an ideal binary surfactant system. Micelles formed in a binary solution have been found to be composed of both surfactants and are in equilibrium with monomeric species in the aqueous phase. The description of the physical behavior of binary surfactant mixtures above the mixed critical micelle concentration (cmc) will depend upon both the value of the cmc and the distribution of surfactant components between micellar and aqueous phases.

The ideal mixing model was first developed by Lange and Beck for a nonionic mixture [16]

and by Lange [17] and Shinoda [18] independently for a homologous ionic surfactant mixture. In the treatments developed by Lange and Shinoda, the mixing in the micelle was assumed to be ideal, i.e., the only contribution to the free energy of mixing comes from the entropy change upon the mixing of the two surfactant species within the micelle. An analytical description which included both micelle composition and monomer concentration above the mixed cmc was developed by Clint [19] for ideal mixing in the micelle.

3.1.2.2 Pseudophase modeling of a nonideal binary surfactant system. Generally, ideal mixing models have been successful in describing the cmc behavior of binary ionic and binary nonionic surfactant mixtures, especially for surfactants with the same hydrophilic groups. When the two surfactants forming a mixed micelle have different head groups, the cmc is not predicted by the ideal theories mentioned above. The so-called regular solution approximation for treating nonideal mixing was first applied by Rubingh to a broad range of different binary mixed surfactant systems [20]. Since there is an argument about the terminology [21], the so-called "regular solution approximation" is referred to as the "Rubingh approximation" in this dissertation. The treatment of Rubingh differs from the ideal treatment in that the interaction between surfactant molecules within the micelle can be included and therefore should provide a better physical description for a wider range of different surfactant combinations. A typical starting point in developing such a model is to consider the chemical potentials of various surfactant species in solution.

At equilibrium the chemical potential of a particular surfactant species is the same everywhere in the system, i.e., the chemical potential of a surfactant in the monomers phase equals to the chemical potential in the micelle phase. Therefore, the chemical potential of the monomeric surfactant component i in the mixed micelle solution can be expressed by

$$\mu_{i} = \mu_{i}^{\circ} + RT \ln C_{i}^{m} \qquad (3.1.2-1)$$

in terms of a standard state chemical potential, μ_i° , and the monomer concentration C_i^{m} , where the activity coefficient of free monomer is assumed to be unity. The chemical potential of component i in the mixed micelle phase is given by

$$\mu_{mi} = \mu_i^{\circ} + RT \ln C_i^{m} = \mu_{mi}^{\circ} + RT \ln f_i x_i \qquad (3.1.2-2)$$

where f_i and x_i are the activity coefficient and the mole fraction of the ith component in the micelle phase, respectively, μ_{mi}° is the chemical potential of component i in pure micelle system, which can be expressed using a phase separation model of micellization as the following:

$$\mu_{\rm mi}^{\circ} = \mu_{\rm i}^{\circ} + RT \ln C_{\rm i}^{\circ} \qquad (3.1.2-3)$$

where C_i° is the cmc of pure component i. Therefore, since $\mu_i = \mu_{mi}$ at equilibrium, from equations (3.1.2-1), (3.1.2-2) and (3.1.2-3), equation (3.1.2-4) can be obtained

$$C_i^{m} = x_i f_i C_i^{\circ} \qquad (3.1.2-4)$$

which gives the monomer concentration of component i in terms of the micellar composition, an activity coefficient and the cmc of the pure component i.

At the mixed cmc (C_{mix}°), the monomer concentration of component i is equal to its total

mole fraction y times its pure cmc, i.e.,

$$C_i^{m} = y_i C_{mix}^{\circ} \qquad (3.1.2-5)$$

Since the sum of mole fractions in the micelle must equal unity, a general result can be obtained by combining equation (3.1.2-4) and (3.1.2-5):

$$1/C_{mix}^{\circ} = \sum y_i / (f_i C_i^{\circ})$$
 (3.1.2-6)

The equation above gives the mixed cmc in terms of the total mole fraction and pure cmc of each surfactant component, and the activity coefficient of each surfactant component in the micelle phase. The expression in equation (3.1.2-6) is a general equation for multicomponent mixed surfactant system. For an ideal system, the activity coefficients f_i 's are unity, which reduces the equation (3.1.2-6) to:

$$1/C_{mix}^{\circ} = \Sigma y_i/C_i^{\circ}$$
 (3.1.2-7)

which is actually the expression derived by Lange and Beck [16] and Clint [19] for the ideal system.

<u>3.1.2.3 Interaction parameter</u>. For an ideal mixed surfactant system, the mixed cmc can be obtained from total mole fractions and pure cmc's. For nonideal systems, however, the activity coefficients must be first determined. Here the Rubingh approximation can be introduced for a binary surfactant system to give the activity coefficients [22] :

$$f_1 = \exp \beta (1 - x_1)^2 \tag{3.1.2-8}$$

$$f_2 = \exp\beta x_1^2 \tag{3.1.2-9}$$

where x_1 is the mole fraction of surfactant 1 in the mixed micelle, β is the so called "interaction parameter", which is dimensionless. An alternative form of interaction parameter, W, with the dimension of energy, can be related to β by

$$\beta = W/RT \qquad (3.1.2-10)$$

where W can be interpreted as a parameter representing an excess free energy of mixing.

To obtain activity coefficients in a binary surfactant system, one must first solve for the micellar fraction x and interaction parameter β . Two relationships can be obtained from equation (3.1.2-4) and (3.1.2-5) for a binary system at mixed cmc:

$$f_1 = y_1 C_{\text{mix}}^{\circ} / (x_1 C_1^{\circ})$$
 (3.1.2-11)

$$f_2 = y_2 C_{mix}^{\circ} / [(1-x_1)C_2^{\circ}]$$
 (3.1.2-12)

Also, β can be related to f_1 and f_2 by rearranging equations (3.1.2-8) and (3.1.2-9):

$$\beta = \ln f_1 / (1 - x_1)^2 = \ln f_2 / x_1^2 \qquad (3.1.2 - 13)$$

By combining equations (3.1.2-11), (3.1.2-12) and (3.1.2-13), β can be related to mixed cmc, pure cmc and micelle fractions as below:

$$\beta = \ln \left[y_1 C_{\text{mix}}^{\circ} / (x_1 C_1^{\circ}) \right] / (1 - x_1)^2 = \ln \left[y_2 C_{\text{mix}}^{\circ} / ((1 - x_1) C_2^{\circ}) \right] / x_1^2$$
(3.1.2-14)

Therefore, x_1 can be solved iteratively from equation (3.1.2-14). β will then be obtained by substituting x_1 back into equation (3.1.2-14). By substituting β into equations (3.1.2-8) and (3.1.2-9), the activity coefficients can be obtained.

<u>3.1.2.4</u> Counterion binding. In the pseudophase model, micelles and the monomeric solution are considered to be two separate phases. For an electrolytic surfactant solution, the micelles form a charged surface. Therefore, a Stern's double layer can be developed on the surface of the micelle phase. The thickness of this double layer is normally assumed to be small compared with the radius of curvature of the micelle surface, and the counterions are distributed homogeneously (and parallel to the micelle surface) on the micelle surface [23]. Therefore, in equation (3.1.2-2), the chemical potential μ_{mi} should be replaced by the electrochemical potential μ_{mi} ', which contains an additional energy term ZNe ψ ,

$$\mu_{mi}' = \mu_{mi}^{\circ} + RT \ln f_1 x_i + ZNe\psi$$
 (3.1.2–15)

where Z is the number of charges of the ion, e is the electronic charge, N is the Avogardro number, and ψ is the electrical potential.

Normally, however, an effective additional energy term $k_i ZNe\psi$ instead of ZNe ψ was used because it was assumed that each ion would contribute less than a charge e to the micelle [23], which changes equations (3.1.2-3) and (3.1.2-2) into:

$$\mu_{mi}^{\circ} = \mu_{i}^{\circ} + RT \ln C_{i}^{\circ} = \mu_{mi}^{\circ} + k_{i} ZNe\psi^{\circ}$$
(3.1.2-16)
$$\mu_{mi}^{\circ} = \mu_{i}^{\circ} + RT \ln C_{i}^{m} = \mu_{mi}^{\circ} + RT \ln f_{i} x_{i} + k_{i} ZNe\psi$$
(3.1.2-17)

where ψ^{o} is the electronic potential of pure micelle phase, ψ is the electronic potential of the mixed micelle phase, and k_i represents the ratio of the number of counterions to long-chain ions in the micelle and is always less than unity.

For a long-chain ionic surfactant of 1:1 type with no added salt [23],

$$\Psi = (RT/NZ_ie) [\ln (2000\pi\sigma^2/DRT) - \ln C_i]$$
 (3.1.2-18)

where D is the dielectric constant, σ is the surface charge density of the micelle and C_i is the total counterion concentration in the solution. By substituting equation (3.1.2-18) into (3.1.2-16) and (3.1.2-17) and rearranging the equations:

$$\ln C_i^{\circ} = A_0 - k_i \ln C_i^{\prime} \qquad (3.1.2-19)$$

$$\ln (C_i^m / f_i x_i) = A_0 - k_i \ln C_i^{"}$$
(3.1.2-20)

where A₀ is $[(\mu_{mi}^{\circ} - \mu_{i}^{\circ})/RT + k_{i} \ln (2000\pi\sigma^{2}/DRT)]$, Ci' and Ci'' are the total concentrations of counterions in the pure and mixed micelle solutions respectively. Combining equations (3.1.2-19), (3.1.2-5) and (3.1.2-20),

$$f_i x_i = (y_i C_{mix}^{\circ} C_i^{\circ}) (C_i^{\circ} C_i^{\circ})^{k_i}$$
 (3.1.2-21)

For a binary system, equation (3.1.2-21) can be combined with (3.1.2-13) to give

$$\beta = \ln \left[(y_1 C_{\text{mix}}^{\circ} / (C_1^{\circ} x_1)) (C_1^{\circ} / (C_1^{\circ})^{k_1} \right] / x_2^2$$

=
$$\ln \left[(y_2 C_{\text{mix}}^{\circ} / (C_2^{\circ} x_2)) (C_2^{\circ} / (C_2^{\circ})^{k_2} \right] / x_1^2 \qquad (3.1.2-22)$$

Various k_i values ranging from 0.4 to 0.8 were published based on both theoretical and experimental results [23, 24] and x_1 and x_2 can be obtained iteratively. The literature values of k_1 and k_2 are available for most of the 1:1 type systems; otherwise, it can be obtained experimentally from equation (3.1.2-19). Then, β can be calculated by substituting x into equation (3.1.2-22).

<u>3.1.2.5 The error of the interaction parameter β </u> Since the interaction parameter β is not an experimental value, the error of β cannot be obtained from normal standard deviation calculation. A method has been developed [25] to calculate the error of β by plotting S, the sum of the square of the difference between the experimental cmc and the calculated cmc, versus β , which is shown in Figure 3.1.2-1, where S can be obtained directly from the BASIC program I in the following section. A parabola is obtained by plotting S against β , and the minimum value is S°. Then, a value S' can be calculated from the equation

$$S' = S^{\circ} [1 + 1/(n-1)],$$
 (3.1.2-23)

where n is the number of experimental cmc's, and marked on the curve. The corresponding value of the interaction parameter β ' gives the error of the interaction parameter β , because $\beta' = \beta + \Delta\beta$ (or $\beta - \Delta\beta$, because the curve is symmetrical).

<u>3.1.2.6 Nonideal pseudophase modeling for the dimeric surfactant systems</u>. The interaction parameter and counterion binding discussed above are all for 1:1 type



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Figure 3.1.2-1 The sum of the square of cmc error, S, versus the interaction parameter β .

electrolytes. For the surfactant with two or more ionic groups, however, the expressions need to be modified. For the surfactant with two ionic groups, such as $R_nCH(COOK)_2$, its cmc is about three times that of its corresponding fatty acid soap [23]. The larger cmc results mainly from its larger electrical repulsive force among the head groups. The corresponding electrical energy per micelle-forming ion becomes i times greater, here i is the number of ionic groups. Then equation (3.1.2-19) changes into:

$$\ln C_i^{\circ} = A_0 - ik_i \ln C_i^{\prime} \qquad (3.1.2-24)$$

Since the dimeric surfactants studied in this work have one ammonium group on each alkyl chain, they also fall into the definition of the surfactants with two ionic groups. However, there is an obvious difference between the dimeric surfactants and the common surfactants with two ionic groups, i.e., instead of being together at one end of the chain, the two ionic groups of the dimeric surfactants are seperated by an alkyl segment. The separation of the two ionic groups makes the chemical environment of each of the ionic groups similar to that of the 1:1 type electrolyte. Therefore, the mixed CTAB and dimeric surfactant system will be treated as a 1:1 type mixture in this work.

Various value of k_i were obtained by Lin [24] experimentally for different compounds at certain temperatures. Among them, 0.60 is the most suitable value for this work, because it was obtained for surfactant n-alkyltrimethylammonium bromides at 60 °C, which is very close to the dimeric systems studied in this work.

Two BASIC programs were used in this work. Program I [26] is for β calculation and program II, which was modified from the original one [22], is for the nonideal mixed cmc

calculation. The two programs are listed as follows:

BASIC Program I - β calculation

- 100 LET SBEST = 10000
- 110 LET KK = 0.6
- 120 LET BETASTEP = 0.01
- 130 DIM Y(100), X(100), CMC(100), CMCPR(100), GAMA(100), GAMB(100),Cl(100)
- 140 CLEAR
- 150 INPUT PROMPT "NUMBER OF DATA SETS? ": N
- 160 READ CMCA0, CMCB0 ! CMCA0 REFERS TO PURE DICATIONIC
- 170 LET X0 = 0
- 180 FOR I = 1 to N
- 190 READ CMC(i), y(i)
- 200 NEXT I
- 210 INPUT PROMPT "INITIAL BETA/ (CHOOSE SMALL) " : BETA
- 220 LET BETA = BETA + BETASTEP
- 230 FOR I = 1 to N
- 240 LET Cl(I) = Y(I)*CMC(I) + (1-Y(I))*2*CMC(I)
- 250 LET CMCA = CMCA0*(Cl(I)/2/CMCA0)^(-KK)
- 260 LET CMCB = CMCB0*(Cl(I)/CMCB0)^(-KK)
- 270 FOR XX = X0 to 1 STEP 0.0001
- 280 LET GAMB(I) = EXP(BETA*(1-XX)*(1-XX))
- 290 LET GAMA(i) = EXP(BETA*XX*XX)
- 300 LET YY = GAMB(I)*XX*CMCB/(GAMA(I)*(1-XX)*CMCA +

GAMB(i)*XX*CMCB)

310 IF YY < Y(I) THEN 360

! PRINT YY,Y(I)

LET X(I) = XX

LET X0 = XX

GO TO 370

NEXT XX

FOR I = 1 to N

LET CMCA = CMCA0 $(Cl(I)/2/CMCA0)^{-KK}$

LET CMCB = CMCB0*(Cl(I)/CMCB0)^(-KK)

IF SETCODE = 1 THEN RETURN

LET $S = S + (CMC(I) - CMCPR(I))^2$

PRINT "S= ";S,"BETA= "; BETA

IF S < SBEST THEN LET SBEST = S

IF S > SBEST THEN 650

 $LET CMCPR(i) = CMCA^{*}(1-X(I))^{*}GAMA(I) + CMCB^{*}X(I)^{*}GAMB(i)$

IF SETCODE < 1 THEN PRINT Y(I), CMC(I), CMCPR(I), X(I)

NEXT I

NEXT I

LET S = 0

NEXT I

PRINT

LET X0 = 0.0001

DATA 0.0438,1.15

FOR I = 1 to N

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360

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- 560 DATA 0.0498, 0.1
- 570 DATA 0.0496,.2
- 580 DATA 0.0562,.3
- 590 DATA 0.0497,.4
- 600 DATA 0.0775,.5
- 610 DATA 0.0756,.6
- 620 DATA 0.1014,.7
- 630 DATA 0.1113,.8
- 645 GO TO 220
- 650 INPUT PROMPT "TO PRINT RESULTS, ENTER Y (RETURN) ": YR\$
- 660 CLEAR
- 670 PRINT
- 680 PRINT
- 690 PRINT "BEST S = "; SBEST; "FOR BETA = " ; BETA -.01
- 700 LET SETCODE = 1
- 710 LET BETA = BETA .01
- 720 GOSUB 380
- 730 PRINT
- 740 PRINT " DEVIATION Y CMC XCALC CMC CALC"
- 750 PRINT
- FOR I = 1 to N
- 770 PRINT CMCPR(i) CMC(I), Y(I);" "; CMC(I), X(I), CMCPR(I)
- 780 NEXT I
- 790 END

BASIC Program II - Mixed cmc calculation,

- 10 REM-CALCULATE BINARY MIXED CMC FROM MICELLAR BETA PARAMETER
- 20 INPUT BETA, Y1, CMC1, CMC2, CMCMAX, Z2
- 30 LET $Y_2 = 1 Y_1$
- 31 LET X1 = 0
- 32 LET X2 = 1
- 33 LET G=(Y1*CMC2/(Y2*CMC1))*(Z2*CMC2/CMC1)^0.6
- 40 FOR I = 1 TO 25
- 50 LET XM1=0.5*(X1+X2)
- 55 LET XM2=1-XM1
- 60 LET F1=EXP(BETA*XM2*XM2)
- 65 LET F2=EXP(BETA*XM1*XM1)
- 70 LET F=G*F2*XM2/(F1*XM1)
- 80 IF F>1 THEN LET X1=XM1
- 82 IF F<1 THEN LET X2=XM1
- 85 IF F=1 THEN GOTO 91
- 90 NEXT I
- 91 LET CM = CMCMAX
- 92 FOR N = 1 TO 5000
- 93 LET CM = CM 0.001
- 94 LET $C1 = (CM^{*}(Y1+Y2^{*}Z2)/CMC1)^{0.6}$
- 95 LET C2 = $(CM*(Y1/Z2+Y2)/CMC2)^{0.6}$
- 96 LET M = CM*(Y1*C1/(F1*CMC1)+Y2*C2/(F2*CMC2))
- 97 IF -0.01<(M-1) and (M-1)<0.01 THEN GOTO 104

- 99** IF (M-1) > 0.01 THEN GOTO 101
- 100** IF (M-1) < -0.01 THEN GOTO 101
- 101 NEXT N
- 104 LET CMCM = CM
- 105 PRINT "F1 = ", F1
- 106 PRINT "F2 = ", F2
- 110 PRINT "MIXED CMC = ", CMCM
- 120 END
- * In program II, cmc1 is the cmc of CTAB, cmc2 is the other surfactant in a binary system, cmcmix is the mixed cmc, and Z2 is the ion number of the second surfactant.
- ** Statements 99 and 100 need to be adjusted according to the required accuracy of the specific system.

3.1.3 Mixed cmc Determination

Since the dimeric surfactants and single chain surfactants studied in this work are all cationic surfactants, conductivity was employed for the measurements of cmc. When the conductivity is plotted versus the concentration, a break in the plot is taken to be the cmc. In previous works, the cmc was obtained by calculating the intersection of two straight lines on both sides of the break. The cmc obtained this way is not very accurate because the break is not sharp for many solutions. To make the cmc calculation more accurate, a new method of calculating the cmc was developed [27].

A curve with two linear asymptotic segments, which is similar to the graphs of the conductivity vs. concentration, is shown in Figure 3.1.3 (a). The first and second

derivatives are shown in Figure 3.1.3 (b) and (c). x_0 , which is the value of x corresponding to the break of the curve, is the cmc in the conductivity graph. In many of the real conductivity graphs, this break is not very sharp so that it can not be determined accurately. Its second derivative, however, shows a very sharp peak as illustrated in Figure 3.1.3 (c). If the second derivative is assumed to have a Lorentzian line shape, namely

$$d^{2}y/dx^{2} = -k_{1} / [(x-x_{0})^{2} + k_{2}^{2}]$$
(3.1.3-1)

where k₁ and k₂ are two constants, the first derivative is obtained by integration to be

$$dy/dx = -(k_1/k_2) \tan^{-1}[(x-x_0)/k_2] - k_3$$
 (3.1.3-2)

where k_3 is another constant. A further integration for equation (3.1.3-2) gives the equation for the graph in Figure 3.1.3 (a) as the following:

$$y = -[k_1(x-x_0)/k_2] \tan^{-1}[(x-x_0)/k_2] + (k_1/2)\log[(x-x_0)^2 + k_2^2] + k_3x + k_4 \quad (3.1.3-3)$$

where k_4 is also a constant from the integration.

Fitting the experimental data (y) to equation (3.1.3-3) by a least squares program, where x is the total surfactant concentration, the value of x_0 can be obtained, and it corresponds to the cmc. Other than the Lorentzian shape, there are also some other assumptions for the second derivatives, such as Gaussian equation. However, the Lorentian assumption is easier to be integrated than the others.



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Figure 3.1.3 Schematic curve of conductivity vs. concentration and its first and second derivatives.

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3.2 Experimental

3.2.1 Materials and Instruments

All the dimeric surfactants and other compounds used in the mixed cmc measurements were the same as those used in the Krafft temperature experiments. The same conductivity meter was also used in the cmc measurements.

3.2.2 Samples preparation

The same stock solutions used in the Krafft temperature experiments were used in the cmc measurements. 10.00 mL aliquots of pure or mixed surfactant samples were made from the stock solutions.

In the mixed cmc measurement, a 10.00 mL sample of the most concentrated solution was made first. The conductivity was then measured with the sample immersed in a 46.5 °C water. A certain time would be allowed for the sample to equilibrate at the bath temperature before the reading was taken. After the first reading was taken, 1.00 mL of the sample was taken out and 1.00 mL of deionized water was added into the sample. The sample was now 10 % diluted. After reading the conductivity again at equilibrium, the sample was diluted the same way consecutively until enough number of readings was taken. Since the concentration of the samples were very small (most of them were smaller than 1 mM), the volume change during the dilution was ignored. Before each reading, the sample would be stirred and equilibrium was made sure to be reached.

3.3 Results and Discussion

3.3.1 Critical Micelle Concentration (cmc) of Pure Dimeric Surfactants

The cmc of CTAB and dimeric surfactants 12-2-12, 14-2-14, 16-2-16, 16-4-16 and 16-6-16 were determined using conductivity measurements at 46.5°C. The reason that the cmc were determined at 46.5 °C is that the Krafft temperature of 16-2-16, which is the highest among all six compounds, is 45 °C as described in chapter 2. To compare the cmc of various compounds, all conductivity measurements were performed at 46.5 °C. The conductivity versus concentration plots are shown in Figure 3.3.1-1. The concentration at the break in the plot for each sufactant solution was obtained by least-squares fitting of the data to equation (3.1.3-3), and is taken as the cmc. The results are listed in Table 3.3.1-1.

Table 3.3.1-1 Cmc of CTAB and m-s-m at 46.5°C

Surfactant	CTAB	12-2-12	14-2-14	16-2-16	16-4-16	16-6-16
cmc, mM	1.15	1.38	0.21	0.034	0.044	0.047
log ₁₀ (cmc/mM)	0.061	0.140	-0.68	-1.47	-1.36	-1.33

From the cmc listed in table 3.3.1-1, it can be seen that chain length has a much more pronounced effect on the cmc than the spacer length does. The cmc of 12-2-12, which has the shortest chain length among the five dimeric surfactants studied, is much larger than the cmc of all four other dimeric surfactants, and close to that of the monomeric surfactant CTAB, which has 16 carbons in the chain. When the number of carbons in the hydrocarbon chain increases from 12 to 14 and to 16 while the spacer is kept same, the cmc



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Figure 3.3.1-1 Conductivity of (a) CTAB (b) 12-2-12 2Br⁻ (c) 14-2-14 2Br⁻ versus concentration at 46.5 °C.

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Figure 3.3.1-1 Conductivity of (d) 16-2-16 2Br- (e) 16-4-16 2Br- (f) 16-6-16 2Br⁻ versus concentration at 46.5 °C.

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decreases from 1.38 to 0.21 and to 0.034 mM, respectively. It is well known that the cmc decreases logarithmically with an increase in the number of carbon atoms m for various surfactants. The relationship between the cmc and the carbon number m can be expressed by equation (3.3.1-1) as follows:

$$\log CMC = A - Bm \tag{3.3.1-1}$$

This empirical equation has been proved to work very well for numerous single chain surfactant systems by many investigators [23]. Normally the values of A are approximately constant for homologs of different numbers of carbon atoms in the hydrocarbon chain and vary with the kinds and number of hydrophilic groups or substituents in the hydrocarbon chain. The values of B, however, are approximately equal to $\log_{10}2$ for most single chain surfactants having one ionic group, but vary with the number of ionic groups, including nonionic agents [23].

To find out if this equation can also be applied to the dimeric surfactants, values of the logarithm of the cmc of dimeric surfactants are also listed in Table 3.3.1-1, and plotted against the number of carbon atoms in the long hydrocarbon chain in the dimeric surfactants (Figure 3.3.1-2). Indeed, a good linear correlation is obtained between log(cmc) and the carbon number *m*. Since the dimeric surfactants studied in this work have two ionic groups, it is not surprising that the value of *B* is 0.40 instead of 0.3 (= $log_{10}2$).

As shown in Table 3.3.1-1, the values of cmc for the three 16-s-16 surfactants also change with the length of the spacers. However, the change in the cmc values with the length of



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Figure 3.3.1-2 Logarithm of the cmc versus the number of carbons in the hydrocarbon chain of m-2-m dimeric surfactants with m = 12, 14 and 16 at 46.5 °C.

increases from 2 to 4 to 6, the cmc only changes from 0.034 to 0.044 to 0.047 mM. It can spacers is much smaller compared with the change with the chain length. When spacer then be concluded from these results that the chain length is the most important factor in the determination of the cmc value for the dimeric surfactants, whereas the spacer only has a small effect on the cmc values.

Zana and his co-workers also determined cmc of m-s-m by conductivity measurements [28]. The only difference between their experiments and ours is the temperature. They did their experiments at 25 °C, while our results were obtained at 46.5 °C. The cmc's obtained by Zana's group are 0.84 mM for 12-2-12, 0.021 mM, 0.027 mM, and 0.043 mM for 16-2-16, 16-4-16 and 16-6-16, respectively. Their results are very close to ours listed in Table 3.3.1-1. According to our Krafft temperature results discussed in chapter 2, the T_k of 16-s-16 compounds are all above the room temperature, and the T_k of 16-2-16 is even as high as 45 °C. However, from our experience, the dimeric solution can stay clear for a long time before it gets cloudy and precipitates eventually. Therefore, the cmc's obtained by Zana's group must have been determined during this "clear time". Even though reasonable results can be obtained during this time, the results are still not reliable, because the solution is actually not at equilibrium. From our experience, reproducible results are not always obtained when the experiments are repeated.

3.3.2 A Single Chain Binary System

To examine the validity of the method used in this work, the mixed cmc values were measured for the binary system CTAB+CPB. The conductivity datas are listed in Table 3.3.2-1, and the graphs of conductivity versus concentrations are shown in Figure 3.3.2-1. The averaged interaction parameter of this system were obtained directly from the BASIC



Figure 3.3.2-1 Conductivity of the binary system CTAB+CPB versus concentration with mole fraction of CTAB (a) 0, (b) 0.1, (c) 0.2, (d) 0.3 at 46.5 °C.



Figure 3.3.2-1 Conductivity of the binary system CTAB+CPB versus concentration with mole fraction of CTAB (e) 0.4, (f) 0.5, (g) 0.6, (h) 0.7 at 46.5 °C.



program I, and the nonideal mixed cmc values were calculated by the BASIC program II listed in section 3.1.2.5. The ideal, nonideal mixed cmc and the averaged interaction parameter β are all summarized in Table 3.3.2-2, and the ideal and nonideal curves are shown in Figure 3.3.2-2. The averaged interaction parameter for this system was obtained from eight experimental mixed cmc's. The data at fraction 0.2 was discarded in the calculation due to its discordance with others in the data set.

Table 3.3.2-2 Nonideality of the binary system CTAB+CPB at 46.5 °C

У	cmc, mM	cmc, mM	cmc, mM	β
(CTAB)	(experimental)	(ideal)	(nonideal)	
1.0	1.15	1.15	1.15	
0.9	1.09	1.11	1.09	
0.8	1.03	1.06	1.04	
0.7	1.00	1.03	1.00	
0.6	0.96	0.99	0.96	
0.5	0.95	0.96	0.93	-0.15±0.05
0.4	0.90	0.93	0.90	
0.3	0.88	0.90	0.88	
0.2	0.82	0.87	0.86	
0.1	0.85	0.84	0.84	
0	0.82	0.82	0.82	



Figure 3.3.2-2 Ideal and nonideal mixed cmc of the binary system "CTAB+CPB" versus mole fraction of CTAB at 46.5 °C.

The mixed cmc graphs shown in Figure 3.3.2-2 shows that the ideal and nonideal curves are very close, which means the CTAB+CPB system is almost ideal. Its big interaction parameter also proves its small nonideality. A comparison between this single chain binary system and the dimeric binary systems will be made in later discussion.

3.3.3 Mixed cmc of CTAB and Dimeric Surfactants Binary Systems

In this work, values of the mixed cmc were determined for five binary systems each containing CTAB and a dimeric surfactant. The five mixed surfactant systems are: CTAB+12-2-12, CTAB+14-2-14, CTAB+16-2-16, CTAB+16-4-16 and CTAB+16-6-16. In addition to the cmc's of pure CTAB and each pure dimeric surfactant, nine mixed cmc values were determined by conductivity measurement for each system at CTAB mole fractions of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9. All the conductivity measurements were made at 46.5 °C. This temperature 46.5 °C was chosen to be slightly above the Krafft temperature of 16-2-16, 45 °C, which is the highest one among all five dimeric surfactants. The mixed cmc results are listed in Table 3.3.3-1. The conductivity data are listed in Table 3A-(a) to 3A-(e) in the Appendix, and the plots of conductivity versus concentration are shown in Figure 3.3.3-1 to 3.3.3-5.

In the plots of conductivity versus concentration in Figure 3.3.3-1 to 3.3.3-5, the data were analyzed the same way as that for the monomeric surfactants. The value of x_0 obtained from fitting each set of data to Equation (3.1.3-3) was assigned to be the mixed cmc. For the binary systems CTAB+12-2-12 and CTAB+14-2-14, the mixed cmc values (Table 3.3.2-1) spread rather evenly between the cmc's of the two pure components. However, for the binary systems CTAB+16-2-16, CTAB+16-4-16, and CTAB+16-6-16, most of the mixed cmc values are close to the lower cmc value of a pure component, i.e., the cmc of



Figure 3.3.3-1 Conductivity of binary systems "CTAB+12-2-12 2Br-" versus concentration with the fraction of CTAB (a) 0.1, (b) 0.2, (c) 0.3 at 46.5 °C.



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Figure 3.3.3-1 Conductivity of binary systems "CTAB+12-2-12 2Br-" versus concentration with the fraction of CTAB (d) 0.4, (e) 0.5, (f) 0.6 at 46.5 °C.

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Figure 3.3.3-1 Conductivity of binary systems "CTAB+12-2-12 2Br-" versus concentration with the fraction of CTAB (g) 0.7, (h) 0.8, (i) 0.9 at 46.5 °C.

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Figure 3.3.3-2 Conductivity of binary systems "CTAB+14-2-14 2Br-" versus concentration with the fraction of CTAB (a) 0.1, (b) 0.2, (c) 0.3 at 46.5 °C.



Figure 3.3.3-2 Conductivity of binary systems "CTAB+14-2-14 2Br-" versus concentration with the fraction of CTAB (d) 0.4, (e) 0.5, (f) 0.6 at 46.5 °C.



Figure 3.3.3-2 Conductivity of binary systems "CTAB+14-2-14 2Br-" versus concentration with the fraction of CTAB (g) 0.7, (h) 0.8, (i) 0.9 at 46.5 °C.

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Figure 3.3.3-3 Conductivity of binary systems "CTAB+16-2-16 2Br-" versus concentration with the fraction of CTAB (a) 0.1, (b) 0.2, (c) 0.3 at 46.5 °C.



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Figure 3.3.3-3 Conductivity of binary systems "CTAB+16-2-16 2Br-" versus concentration with the fraction of CTAB (d) 0.4, (e) 0.5, (f) 0.6 at 46.5 °C.

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Figure 3.3.3-3 Conductivity of binary systems "CTAB+16-2-16 2Br-" versus concentration with the fraction of CTAB (g) 0.7, (h) 0.8, (i) 0.9 at 46.5 °C.



Figure 3.3.3-4 Conductivity of binary systems "CTAB+16-4-16 2Br-" versus concentration with the fraction of CTAB (a) 0.1, (b) 0.2, (c) 0.3 at 46.5 °C.



Figure 3.3.3-4 Conductivity of binary systems "CTAB+16-4-16 2Br-" versus concentration with the fraction of CTAB (d) 0.4, (e) 0.5, (f) 0.6 at 46.5 °C.



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Figure 3.3.3-4 Conductivity of binary systems "CTAB+16-4-16 2Br-" versus concentration with the fraction of CTAB (g) 0.7, (h) 0.8, (i) 0.9 at 46.5 °C.



Figure 3.3.3-5 Conductivity of binary systems "CTAB+16-6-16 2Br-" versus concentration with the fraction of CTAB (a) 0.1, (b) 0.2, (c) 0.3 at 46.5 °C.



Figure 3.3.3-5 Conductivity of binary systems "CTAB+16-6-16 2Br-" versus concentration with the fraction of CTAB (d) 0.4, (e) 0.5, (f) 0.6 at 46.5 °C.





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16-s-16. The mixed cmc values start to increase dramatically only when the fraction of CTAB is close to 0.9. These results indicate that the surfactant 16-s-16 can easily partition into the micelles formed by CTAB, but the CTAB molecules do not partition well into the micelles of dimeric surfactant 16-s-16. This is similar to the results obtained from the Krafft temperature experiments in Chapter 2. A quantitative treatment is given in the next section.

Fraction of CTAB		Mixed cmc, mM				
y (CTAB)	CTAB+ 12-2-12	CTAB+ 14-2-14	CTAB+ 16-2-16	CTAB+ 16-4-16	CTAB+ 16-6-16	
1.0	1.15	1.15	1.15	1.15	1.15	
0.9	1.13	0.86	0.12	0.25	0.65	
0.8	1.14	0.47	0.085	0.11	0.13	
0.7	1.13	0.41	0.071	0.10	0.082	
0.6	1.12	0.34	0.060	0.076	0.080	
0.5	1.14	0.31	0.068	0.078	0.076	
0.4	1.18	0.27	0.054	0.050	0.067	
0.3	1.15	0.26	0.056	0.056	0.063	
0.2	1.19	0.23	0.050	0.050	0.055	
0.1	1.23	0.19	0.038	0.050	0.054	
0	1.38	0.20	0.034	0.044	0.047	

Table 3.3.3-1 Mixed cmc of CTAB+m-s-m Binary Systems at 46.5 °C

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3.3.4 Nonideality of CTAB and Dimeric surfactants Binary Systems

Even if the monomer phase in a micelle solution is considered to be ideal, the micelle phase may be nonideal. The activity coefficient of a nonideal micellar solution is smaller than one. The nonideality can be expressed by an interaction parameter β , which represent the free energy of mixing. For most of the systems where hydrocarbon chains mix inside the hydrophobic micelle core, β is negative. The negative β value also means that the energy level is lowered when the single hydrocarbon chain moves from monomer phase to the micelle phase.

The ideal mixed cmc can be obtained from equation (3.1.2-7). The nonideal mixed cmc can be obtained from equation (3.1.2-22) by using the pseudophase nonideal model with considering the counterion effect as well. In considering the counterion effect in the nonideal model, the dimeric surfactants are treated as a 1:1 type electrolyte. The reason for doing so is that even though there are two ionic groups in a dimeric surfactant molecule, the two groups are separated by a spacer. Therefore, the electrical repulsive force around each ionic group is still similar to a 1:1 type electrolyte, and the value of $K_i = 0.6$ obtained for *n*-alkyltrimethyl ammonium salts [24] was used for the nonideal model calculation of all five binary systems. By using the theory discussed in section 3.1.2, all five binary surfactant systems studied in this work were treated with both ideal and nonideal models, and the results are presented in the following sections.

<u>3.3.4.1 CTAB+12-2-12 and CTAB+14-2-14 systems</u>. The ideal and nonideal models were applied to these two systems and the mixed cmc calculated from both models are listed in Table 3.3.4-1 and Table 3.3.4-2.

Fraction of CTAB y (CTAB)	cmc, mM (ideal)	cmc, mM (nonideal)	Interaction Parameter β
1.0	1.15	1.15	
0.9	1.17	1.14	
0.8	1.19	1.13	
0.7	1.21	1.12	
0.6	1.23	1.12	
0.5	1.26	1.13	-0.35±0.07
0.4	1.28	1.15	
0.3	1.30	1.18	
0.2	1.33	1.22	
0.1	1.35	1.28	
0	1.38	1.33	

Table 3.3.4-1Ideal and Nonideal Mixed cmc and the Averaged InteractionParameter for System "CTAB+12-2-12 2Br-" at 46.5 °C

Fraction of CTAB y (CTAB)	cmc, mM (ideal)	cmc, mM (nonideal)	Interaction Parameter β
1.0	1.15	1.15	
0.9	0.78	0.62	
0.8	0.59	0.47	
0.7	0.47	0.40	
0.6	0.40	0.34	
0.5	0.34	0.31	-1.04±0.10
0.4	0.30	0.28	
0.3	0.27	0.25	
0.2	0.24	0.23	
0.1	0.22	0.22	
0	0.20	0.20	

Table 3.3.4-2Ideal and Nonideal Mixed cmc and the Averaged InteractionParameter for System "CTAB+14-2-14 2Br-" at 46.5 °C

The mixed cmc from ideal and nonideal models are also plotted against the fraction of CTAB, which are shown in Figure 3.3.4-1 and Figure 3.3.4-2. For each fraction, the ideal mixed cmc can be obtained from equation (3.1.2-7) by knowing the pure cmc values of CTAB and 12-2-12 or 14-2-14, which are shown by the dotted line in Figure 3.3.4-1 and Figure 3.3.4-2.

The averaged interaction parameters of the binary systems were calculated directly by using the BASIC program I listed in section 3.1.2.6 and the errors were calculated by using the method discussed in section 3.1.2.4. A β value of -0.38±0.07 was obtained for system CTAB+12-2-12 by using all nine sets of experimental mixed cmc values. For system CTAB+14-2-14, however, only eight sets of experimental mixed cmc values were used for calculating the averaged interaction parameter. Because as shown in Figure 3.3.4-2, experimental mixed cmc at fraction 0.9 was discordant from the group so that it was discarded when calculating the averaged β . The overall interaction parameter β , -0.38 and -1.04, were then used for the nonideal mixed cmc calculation with the BASIC program II listed in section 3.1.2.5.

The nonideal mixed cmc values are shown in Figure 3.3.4-1 and Figure 3.3.4-2 by the solid lines. As shown in Figure 3.3.4-1 and Figure 3.3.4-2, the experimental cmc values distribute evenly on both sides of the nonideal cmc curves. Therefore, the obtained interaction parameter β , -0.38±0.07 and -1.04±0.1, can be used to represent the nonideality of the two binary surfactant systems, respectively. Compared with the ideal and nonideal cmc curves of system CTAB + CPB shown in Figure 3.3.2-2, it is obvious that the dimeric binary systems CTAB+12-2-12 and CTAB+14-2-14 deviate more significantly from the ideality. The interaction parameters -0.38 and -1.04 for systems



Figure 3.3.4-1 Ideal and nonideal mixed cmc of binary system "CTAB+12-2-12 2Br-" versus the fraction of CTAB at 46.5 °C.



Figure 3.3.4-2 Ideal and nonideal mixed cmc of binary system "CTAB+14-2-14 2Br-" versus the fraction of CTAB at 46.5 °C.

CTAB+12-2-12 and CTAB+14-2-14 compared with the value -0.15 for CTAB+CPB are a quantitative comparison of the nonideality.

<u>3.3.4.2</u> systems CTAB+16-2-16, CTAB+16-4-16 and CTAB+16-6-16 The mixed cmc values using the ideal and nonideal models were also calculated for these three systems similarly to the two other binary systems, and the results are listed in Table 3.3.4-3, 3.3.4-4 and 3.3.4-5. The ideal and nonideal curves are shown in Figure 3.3.4-3 to 3.3.4-5. Similarly to the two other systems, the dotted lines represent values calculated from the ideal mixed cmc model, and the solid lines represent values calculated from the nonideal mixed cmc model.

Just like the two systems discussed above, the overall interaction parameters and nonideal mixed cmc curves were calculated from program I and II and are shown in Figure 3.3.4-3 to 3.3.4-5. All nine sets of data were used in the β calculation for CTAB+16-2-16 system. For systems CTAB+16-4-16 and CTAB+16-6-16, however, the mixed cmc values at the faction of CTAB 0.9 were discarded due to their discordance with other data. Compared Figure 3.3.4-1, 2 with Figure 3.3.4-3, 4, 5, it can be seen that the mixed cmc for the two systems with shorter chain length are distributed evenly between two pure cmcs. For the systems with 16 carbon chain length, however, most of the mixed cmc values are close to the pure dimeric cmc value, which means that the dimeric surfactant CTAB. In the three Figures 3.3.4-3 to 3.3.4-5, the behavior of CTAB+16-s-16 is seen to deviate more from ideality (with $\beta = -4.19\pm0.5$, -3.57 ± 0.4 and -3.69 ± 0.4 , respectively) than the two binary systems with shorter chain length and the single chain binary system CTAB+CPB. The overall interaction parameters for all six systems are summarized in Table 3.3.4-6.

Fraction of CTAB y (CTAB)	cmc, mM (ideal)	cmc, mM (nonideal)	Interaction Parameter ß
1.0	1.15	1.15	
0.9	0.269	0.12	
0.8	0.152	0.087	
0.7	0.106	0.070	
0.6	0.081	0.060	
0.5	0.066	0.052	-4.19±0.50
0.4	0.056	0.047	
0.3	0.048	0.042	
0.2	0.042	0.039	
0.1	0.038	0.036	
0	0.034	0.034	

Table 3.3.4-3Ideal and Nonideal Mixed cmc and the Averaged InteractionParameter for System "CTAB+16-2-16 2Br-" at 46.5 °C

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Fraction of CTAB y (CTAB)	cmc, mM (ideal)	cmc, mM (nonideal)	Interaction Parameter β
1.0	1.15	1.15	
0.9	0.33	0.16	
0.8	0.19	0.12	
0.7	0.13	0.092	
0.6	0.10	0.078	
0.5	0.085	0.068	-3.57±0.40
0.4	0.072	0.061	
0.3	0.062	0.055	
0.2	0.054	0.051	
0.1	0.049	0.047	
0	0.044	0.044	

Table 3.3.4-4Ideal and Nonideal Mixed cmc and the InteractionParameter for System "CTAB+16-4-16 2Br-" at 46.5 °C

Fraction of CTAB y (CTAB)	cmc, mM (ideal)	cmc, mM (nonideal)	Interaction Parameter β
1.0	1.15	1.15	
0.9	0.34	0.17	
0.8	0.20	0.12	
0.7	0.14	0.096	
0.6	0.11	0.081	
0.5	0.090	0.071	-3.69±0.40
0.4	0.076	0.064	
0.3	0.066	0.058	
0.2	0.058	0.053	
0.1	0.052	0.050	
0	0.047	0.047	

Table 3.3.4-5 Ideal and Nonideal Mixed cmc and the Averaged InteractionParameter for System "CTAB+16-6-16 2Br-" at 46.5 °C

Table 3.3.4-6Averaged Interaction Parameter forCTAB+CPB and CTAB+m-s-m Binary Systems at 46.5 °C

m-s-m (CPB) 12-2-12 14-2-14 16-2-16 16-4-16 16-6-16 β -0.15±0.05 -0.38±0.07 -1.04±0.10 -4.19±0.50 -3.57±0.40 -3.69±0.40



Figure 3.3.4-3 Ideal and nonideal mixed cmc of binary system "CTAB+16-2-16 2Br-" versus mole fraction of CTAB at 46.5 °C.



Figure 3.3.4-4 Ideal and nonideal mixed cmc of binary system "CTAB+16-4-16 2Br-" versus mole fraction of CTAB at 46.5 °C.



Figure 3.3.4-5 Ideal and nonideal mixed cmc of binary system "CTAB+16-6-16 2Br-" versus mole fraction of CTAB at 46.5 °C.

Compared with the interaction parameters for systems CTAB+m-s-m, the β value of -0.15 for CTAB+CPB system is less negative than those for all other systems, i.e., the nonideality of the CTAB+CPB system is the smallest. The nonideality represented by β for the binary systems studied in this work has the trend: CTAB+CPB < CTAB+12-2-12 < CTAB+14-2-14 < CTAB+16-4-16 ≈ CTAB+16-6-16 < CTAB+16-2-16.

In summary, the nonideality of binary CTAB+m-s-m systems increases with the carbon chain length of the dimeric surfactant. The number of carbons in the chain length can also be related linearly with the logarithm of cmc. For dimeric surfactants m-2-m, when the number of carbons in the hydrocarbon chain increases from 12 to 16, the interaction parameter decreases from -0.38 to -4.19. However, when the spacer of the dimeric surfactant increases from 2 to 6 while the chain length is kept the same, the nonideality only decreases slightly. As a matter of fact, the nonideality of the systems 16-4-16 and 16-6-16 can be considered to be the same within experimental error. Because the interaction parameter represents the extra free energy of mixing, it is not surprising that system CTAB+16-2-16 deviates most significantly from ideality. Due to its short spacer, 16-2-16 should have the most compact microstructure. Therefore, more energy must be needed when CTAB molecules form mixed micelles with 16-2-16 aggregates. From another point of view, CTAB prefers to form spherical micelles but 16-2-16 prefers to form worm-like micelles [28], and this difference can account for the large deviation from ideality when the two surfactants are mixed. The tendency to form worm-like micelles decreases in the order $16-2-16 > 16-4-16 \approx 16-6-16 > 14-2-14 > 12-2-12$, and the non-ideality of their mixed micelle systems with CTAB changes correspondingly. Finally, the success of the 1:1 type approximation indicates that in considering the counterion effects for the dimeric binary systems, the environment of the ionic groups in the dimeric surfactants may be similar to that of normal monomeric surfactants.

Bibliography

- 1. P. M. Hollard, Adv. Colloid Interface Sci. 1986, 26, 111.
- 2. W. Guo, E. K. Guzman, S. D. Heavin, Z. Li, B. M. Fung, and S. D. Christian, Langmuir, 1992, 8, 2368-2375.
- G. Zhao and B. Zhu, In *Phenomena in Mixed Surfactant Systems*; J. F. Scamehorn Ed.; ACS Symposium Series 311, American Chemical Society: Washington, DC, 1986; pp 184-198.
- 4. K. Shinoda, E. Hutchinson, J. Phys. Chem. 1962, 66, 577.
- R. F. Kamrath, E. I. Franses, In *Phenomena in Mixed Surfactant Systems*; J. F. Scamehorn Ed.; ACS Symposium Series 311, American Chemical Society: Washington, DC, 1986; pp 44-66.
- 6. R. F. Kamrath, E. I. Franses, J. Phys. Chem. 1984, 88, 1642.
- 7. S. Wall, C. Elvingson, J. Phys. Chem. 1985, 89, 2695.
- 8. M. M. Stecker, G. B. Benedek, J. Phys. Chem. 1984, 88, 6519.
- 9. I. Szleifer, A. Ben-Shaul, W. M. Gelbart, J. Chem. Phys. 1987, 86, 7094.
- 10. R. Nagarajan, Langmuir 1985, 1, 331.
- 11.R. Nagarajan, in Mixed Surfactant Systems, P. Holland and D. Rubingh ed.; ACS Symposium Series 501, American Chemical Society: Washington DC, 1992; Chapter 4.
- J. F. Scamehorn, In *Phenomena in Mixed Surfactant Systems*; J. F. Scamehorn Ed.;
 ACS Symposium Series 311, American Chemical Society: Washington, DC, 1986; pp 1-27.
- M. J. Rosen, In Phenomina in Mixed Surfactant Systems; J. F. Scamehorn Ed.; ACS Symposium Series 311, American Chemical Society: Washington, DC, 1986; pp 144-

162.

- 14. P. M. Holland, D. N. Rubingh, In *Cationic Surfactants: Physical Chemistry*; D. N. Rubingh; P. M. Holland, Eds.; Surfactant Science Series 37; Marcel Dekker, Inc.: New York, NY, 1990; pp 141-187.
- 15. L. Benjamin, J. Phys. Chem. 1964, 68, 3575;
- 16. H. Lange and K. H. Beck, Koloid Z.-Z. Polym. 1973, 251, 424
- 17. H. Lang, Kolloid Z.-Z. Polym. 1953, 131, 96.
- 18. K. Shinoda, J. Phys. Chem. 1954, 58, 541.
- 19. J. Clint, J. Chem. Soc. 1975, 71, 1327.
- 20. D. N. Rubingh, In Solution Chemistry of Surfactants; Mittal, K. L. ed.; Plenum Press, New York, NY, 1979, Vol. 3; pp 337-354.
- 21 S. D. Christian, E. E. Tucker, and J. F. Scamehorn, in *Mixed Surfactant Systems*, P.
 Holland and D. Rubingh ed.; ACS Symposium Series, American Chemical Society:
 Washington DC, 1992; Chapter 3.
- 22. D. N. Rubingh, in *Mixed Surfactant Systems*, P. Holland and D. Rubingh ed.; ACS Symposium Series, American Chemical Society: Washington DC, 1992; Chapter 1.
- 23. K. Shinoda, "Colloidal Surfactants"; Academic: New York, 1963, Chap. 1.
- 24. I. J. Lin and P. Somasundaran, J. Colloid Interface Sci., 1971, 39, 731.
- 25. S. D. Christian, J. Chem. Edu., 1965, 42, 604.
- 26. S. D. Christian, unpublished.
- 27. B. M. Fung, to be published.
- 28. R. Zana, M. Benrraou, and R. Rueff, Langmuir, 1991, 7, 1072-1075.
- 29. D. Danino, A. Kaplun, Y. Talmon, and R. Zana, Cryo-Transmission Electron Microscopy Investigations of Unusual Amphiphilic Systems in Relation to Their Rheological Properties in "Structure and Flow in Surfactant Solutions", ACS symposium series 578, C. A. Herb and R. K. Prud'homme, Ed., 1994.

Appendix

Table 3A Conductivity of Pure CTAB at Various Concentration at 46.5 °C

Conc., mM	κ, mS/cm
3.00	1.83
2.70	1.74
2.43	1.66
2.19	1.58
1.97	1.52
1.77	1.45
1.59	1.39
1.44	1.34
1.29	1.29
1.16	1.23
1.05	1.14
0.941	1.03
0.847	0.937
0.763	0.846
0.686	0.767
0.618	0.693

Table 3A-(a) Conductivity of Binary System CTAB+12-2-12 2Br⁻ at 46.5 °C

y (CTAB) = 0		y (CTAB	() = 0.1
conc. _{tot} , mM	κ, mS/cm	conc. _{tot} , mM	κ, mS/cm
3.00	6.28	3.00	5.72
2.70	5.78	2.70	5.33
2.43	5.43	2.43	4.97
2.19	5.08	2.19	4.64
1.97	4.75	1.97	4.36
1.77	4.45	1.77	4.09
1.59	4.19	1.59	3.85
1.44	3.91	1.44	3.62
1.29	3.61	1.29	3.40
1.16	3.30	1.16	3.14
1.05	3.00	1.05	2.87
0.941	2.74	0.941	2.63
0.847	2.49	0.847	2.40
0.763	2.27	0.763	2.20
0.686	2.06	0.686	2.00
0.618	1.88	0.618	1.82
0.556	1.71	0.556	1.65

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	Table 3A-(a)	Conductivity	y of Binary S	ystem CTAB	8+12-2-12 2Br	⁻ at 46.5 °C
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y (CTAB) = 0.2		y (CTAB) = 0.3
conc. _{tot} , mM	κ, mS/cm	conc. _{tot} , mM	κ, mS/cm
3.00	5.41	3.00	4.83
2.70	5.00	2.70	4.49
2.43	4.67	2.43	4.19
2.19	4.37	2.19	3.94
1.97	4.10	1.97	3.69
1.77	3.85	1.77	3.46
1.59	3.61	1.59	3.26
1.44	3.41	1.44	3.09
1.29	3.20	1.29	2.91
1.16	2.98	1.16	2.73
1.05	2.73	1.05	2.51
0.941	2.48	0.941	2.29
0.847	2.26	0.847	2.08
0.763	2.06	0.763	1.89
0.686	1.87	0.686	1.72
0.618	1.70	0.618	1.56
0.556	1.55	0.556	1.42
0.500	1.41	0.500	1.29
0.450	1.28	0.450	1.17

Table $3A_{-}(a)$	Conductivity of Rinary System CTAR+12-2-12 2Rr at 46.5	°C
	Conductivity of Dinary System CIAD+12-2-12 2D1 at 40.5	C

y (CTAE	B) = 0.4	y (CTAE	B) = 0.5
conc. _{tot} , mM	κ, mS/cm	conc. _{tot} , mM	κ, mS/cm
3.00	4.50	3.00	3.97
2.70	4.18	2.70	3.70
2.43	3.90	2.43	3.46
2.19	3.65	2.19	3.25
1.97	3.43	1.97	3.06
1.77	3.22	1.77	2.89
1.59	3.03	1.59	2.73
1.44	2.88	1.44	2.59
1.29	2.69	1.29	2.44
1.16	2.51	1.16	2.29
1.05	2.30	1.05	2.11
0.941	2.09	0.941	1.92
0.847	1.90	0.847	1.7479
0.763	1.74	0.763	1.60
0.686	1.57	0.686	1.44
0.618	1.42	0.618	1.31
0.556	1.29	0.556	1.19
0.500	1.17	0.500	1.07

y (CTAB) = 0.6		y (CTAB) = 0.7	
conc. _{tot} , mM	κ, mS/cm	conc. _{tot} , mM	κ, mS/cm
2 0000	6102	3 00	2 0062
3.0000	.0192	5.00	2.0902
2.7000	3.3472	2.70	2.8974
2.4300	3.138	2.43	2.7301
2.1870	2.9602	2.19	2.5732
1.9680	2.7824	1.97	2.4372
1.7710	2.6255	1.77	2.3012
1.5940	2.4895	1.59	2.1861
1.4350	2.3535	1.44	2.0711
1.2910	2.228	1.29	1.9717
1.1620	2.091	1.16	1.8702
1.0460	1.9393	1.05	1.7437
0.94100	1.7824	0.941	1.5711
0.84700	1.6025	0.847	1.4278
0.76300	1.4539	0.763	1.2929
0.68600	1.319	0.686	1.1705
0.61800	1.1998	0.618	1.0586
0.55600	1.092	0.556	0.96337
0.50000	0.987		

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Table 3A-(a)	Conductivity	v of Binarv	System	CTAB+12-2-12 2	2 Br⁻ at 4	46.5 °C

y (CTAB) = 0.8		y (CTAB) = 0.9		
cmc _{tot} , mM	κ, mS/cm	cmc _{tot} , mM	κ, mS/cm	
3.0000	2.751	3.00	2.2384	
2.7000	2.5941	2.70	2.1129	
2.4300	2.4372	2.43	2.0062	
2.1870	2.3012	2.19	1.9048	
1.9680	2.1861	1.97	1.8096	
1.7710	2.0721	1.77	1.728	
1.5940	1.9696	1.59	1.6485	
1.4350	1.8723	1.44	1.5753	
1.2910	1.7834	1.29	1.5073	
1.1620	1.6935	1.16	1.4456	
1.0460	1.5659	1.05	1.3305	
0.94100	1.4247	0.941	1.2071	
0.84700	1.2929	0.847	1.1004	
0.76300	1.1705	0.763	0.99265	
0.68600	1.0606	0.686	0.89642	
0.61800	0.96441	0.618	0.81379	
0.55600	0.87655	0.556	0.73429	
0.50000	0.79182	0.500	0.66107	

conc. _{tot} , mM	κ, mS/cm	conc. _{tot} , mM	κ, mS/cm
0.787	1.19	0.106	0.289
0.709	1.11	0.0957	0.262
0.638	1.03	0.0861	0.235
0.574	0.957	0.0775	0.214
0.517	0.892	0.0698	0.190
0.465	0.839	0.0628	0.173
0.418	0.786	0.0565	0.155
0.377	0.743		
0.339	0.699		
0.305	0.660		
0.275	0.623		
0.247	0.583		
0.222	0.546		
0.2	0.502		
0.18	0.461		
0.162	0.424		
0.146	0.385		
0.131	0.348		
0.118	0.318		

with y (CTAB) = 0.1

conc. _{tot} , mM	κ, mS/cm	conc. _{tot} , mM	κ, mS/cm
0.787	1.20	0.106	0.282
0.709	1.12	0.0957	0.256
0.638	1.04	0.0861	0.230
0.574	0.981	0.0775	0.206
0.517	0.904	0.0698	0.186
0.465	0.846	0.0628	0.167
0.418	0.805	0.0565	0.152
0.377	0.745		
0.339	0.700		
0.305	0.660		
0.275	0.618		
0.247	0.583		
0.222	0.538		
0.2	0.491		
0.18	0.457		
0.162	0.412		
0.146	0.382		
0.131	0.343		
0.118	0.314		

with y (CTAB) = 0.2

conc. _{tot} , mM	κ, mS/cm	conc. _{tot} , mM	κ, mS/cm
0.709	1.0575	0.0957	0.234
0.638	0.9801	0.0861	0.212
0.574	0.92153	0.0775	0.191
0.517	0.85667	0.0698	0.171
0.465	0.80647	0.0628	0.153
0.418	0.75626	0.0565	0.137
0.377	0.71442		
0.339	0.67572		
0.305	0.63597		
0.275	0.60668		
0.247	0.56275		
0.222	0.51882		
0.2	0.47698		
0.18	0.432		
0.162	0.39434		
0.146	0.35355		
0.131	0.32008		
0.118	0.28765		
0.106	0.26045		

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with y (CTAB) = 0.3

conc. _{tot} , mM	κ, mS/cm	conc. _{tot} , mM	κ, mS/cm
1.08	1.39	0.146	0.337
0.972	1.28	0.131	0.300
0.875	1.18	0.118	0.270
0.787	1.10	0.106	0.242
0.709	1.02	0.0957	0.219
0.638	0.956	0.0861	0.198
0.574	0.891	0.0775	0.181
0.517	0.842	0.0698	0.161
0.465	0.786		
0.418	0.738		
0.377	0.699		
0.339	0.652		
0.305	0.614		
0.275	0.577		
0.247	0.536		
0.222	0.483		
0.2	0.439		
0.18	0.397		
0.162	0.364		

conc. _{tot} , mM	κ, mS/cm	conc. _{tot} , mM	κ, mS/cm
1.08	1 31	0 146	0 312
0.972	1.22	0.131	0.280
0.875	1.14	0.118	0.251
0.787	1.06	0.106	0.226
0.709	0.985	0.0957	0.204
0.638	0.917	0.0861	0.184
0.574	0.864	0.0775	0.166
0.517	0.810		
0.465	0.761		
0.418	0.722		
0.377	0.675		
0.339	0.635		
0.305	0.597		
0.275	0.552		
0.247	0.504		
0.222	0.467		
0.2	0.420		
0.18	0.380		
0.162	0.344		

conc. _{tot} , mM	κ, mS/cm	conc. _{tot} , mM	κ, mS/cm
1.08	1.29	0.146	0.291
0.972	1.20	0.131	0.264
0.875	1.12	0.118	0.236
0.787	1.04	0.106	0.216
0.709	0.974	0.0957	0.200
0.638	0.908	0.0861	0.176
0.574	0.855		
0.517	0.799		
0.465	0.747		
0.418	0.709		
0.377	0.661		
0.339	0.613		
0.305	0.565		
0.275	0.522		
0.247	0.476		
0.222	0.429		
0.2	0.393		
0.18	0.361		
0.162	0.321		

with y(CTAB) = 0.6

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conc. _{tot} , mM	κ, mS/cm	conc. _{tot} , mM	κ, mS/cm
1.08	1.23	0.146	0.263
0.972	1.15	0.131	0.237
0.875	1.06	0.118	0.214
0.787	0.995	0.106	0.194
0.709	0.926	0.0957	0.174
0.638	0.868	0.0861	0.155
0.574	0.813		
0.517	0.761		
0.465	0.715		
0.418	0.670		
0.377	0.627		
0.339	0.575		
0.305	0.538		
0.275	0.483		
0.247	0.437		
0.222	0.396		
0.2	0.357		
0.18	0.322		
0.162	0.291		

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conc. _{tot} , mM	κ, mS/cm	conc. _{tot} , mM	κ, mS/cm
1.08	1.21	0.146	0.242
0.972	1.13	0.131	0.219
0.875	1.04	0.118	0.200
0.787	0.969	0.106	0.178
0.709	0.910		
0.638	0.847		
0.574	0.794		
0.517	0.741		
0.465	0.687		
0.418	0.640		
0.377	0.587		
0.339	0.530		
0.305	0.481		
0.275	0.447		
0.247	0.401		
0.222	0.361		
0.20	0.327		
0.18	0.296		
0.162	0.266		

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conc. _{tot} , mM	κ, mS/cm	conc. _{tot} , mM	κ, mS/cm
1.08	1.17	0.131	0.191
0.972	1.10	0.118	0.176
0.875	1.02	0.106	0.158
0.787	0.948		
0.709	0.888		
0.638	0.822		
0.574	0.764		
0.517	0.706		
0.465	0.652		
0.418	0.595		

with y (CTAB) = 0.8

0.377

0.339

0.305

0.275

0.247

0.222

0.200

0.180

0.162

0.146

0.542

0.491

0.446

0.404

0.360

0.326

0.297

0.268

0.241

conc. _{tot} , mM	κ, mS/cm	conc. _{tot} , mM	κ, mS/cm
1.08	1.85	0.146	0.466
0.972	1.751	0.131	0.422
0.875	1.67	0.118	0.381
0.787	1.58	0.106	0.344
0.709	1.50		
0.638	1.42		
0.574	1.35		
0.517	1.29		
0.465	1.21		
0.418	1.13		
0.377	1.06		
0.339	0.979		
0.305	0.905		
0.275	0.835		
0.247	0.761		
0.222	0.689		
0.2	0.623		
0.18	0.569		
0.162	0.517		

with y(CTAB) = 0

conc. _{tot} , mM	κ, μS/cm	conc. _{tot} , mM	κ, μS/cm
0 172	275 1	0 0233	71 1
0.155	254.2	0.0209	65.9
0.139	235.4	0.0188	60.7
0.126	217.6		
0.113	200.8		
0.102	186.2		
0.0915	173.6		
0.0824	163.2		
0.0741	152.7		
0.0667	143.3		
0.0600	134.9		
0.054	126.6		
0.0486	118.2		
0.0438	111.9		
0.0394	104.6		
0.0355	97.3		
0.0319	91.0		
0.0287	83.7		
0.0258	77.4		

conc. _{tot} , mM	κ, μS/cm	conc. _{tot} , mM	κ, μS/cm
0.172	268.8	0.0233	70.1
0.155	247.9	0.0209	63.8
0.139	229 1	0.0188	57.5
0.126	212.3	0.0100	57.5
0.120	212.5		
0.113	19/./		
0.102	183.1		
0.0915	171.5		
0.0824	159.0		
0.0741	149.6		
0.0667	141.2		
0.06	132.8		
0.054	125.5		
0.0486	117.2		
0.0438	110.9		
0.0394	103.6		
0.0355	95.2		
0.0319	88.9		
0.0287	82.6		
0.0258	76.4		

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conc. _{tot} , mM	κ, μS/cm	conc. _{tot} , mM	κ, μS/cm
0.101	000 0	0.0050	
0.191	280.3	0.0258	65.9
0.172	257.3	0.0233	59.6
0.155	235.4	0.0209	54.4
0.139	217.6	0.0188	50.2
0.126	200.8		
0.113	185.1		
0.102	172.6		
0.0915	160.0		
0.0824	149.6		
0.0741	139.1		
0.0667	130.8		
0.06	122.4		
0.054	115.1		
0.0486	106.7		
0.0438	99.4		
0.0394	92.1		
0.0355	84.7		
0.0319	78.5		
0.0287	72.2		

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conc. _{tot} , mM	κ, μS/cm	conc. _{tot} , mM	κ, μS/cm
0.191	268.8	0.0233	57.5
0.172	246.9	0.0209	52.3
0.155	225.9	0.0188	48.1
0.139	209.2		
0.126	193.5		
0.113	178.9		
0.102	166.3		
0.0915	154.8		
0.0824	144.4		
0.0741	134.9		
0.0667	125.5		
0.06	117.2		
0.054	109.8		
0.0486	102.5		
0.0438	95.2		
0.0394	87.9		

with y (CTAB) = 0.3

81.6

75.3

68.0

62.8

0.0355

0.0319

0.0287

conc. _{tot} , mM	κ, μS/cm	conc. _{tot} , mM	κ, μS/cm
0.324	427.0	0.0428	97.0
0.324	437.2	0.0438	07.9
0.292	399.6	0.0394	80.5
0.262	365.1	0.0355	73.2
0.236	333.7	0.0319	68.0
0.213	306.5	0.0287	61.7
0.191	280.3	0.0258	56.5
0.172	256.3	0.0233	51.3
0.155	236.4	0.0209	47.1
0.139	217.6	0.0188	42.9
0.126	199.8		
0.113	185.1		
0.102	171.5		
0.0915	159.0		
0.0824	147.5		
0.0741	132.8		
0.0667	119.2		
0.06	113.0		
0.054	103.6		
0.0486	95.2		

conc. _{tot} , mM	κ, μS/cm	conc. _{tot} , mM	κ, μS/cm
0.4	486 4	0.054	102.5
0.4	443 5	0.0486	94 1
0.324	407.9	0.0438	85.8
0.292	372.4	0.0394	78.5
0.262	340.0	0.0355	72.2
0.236	310.7	0.0319	65.9
0.213	283.5	0.0287	59.6
0.191	259.4	0.0258	55.4
0.172	237.4	0.0233	50.2
0.155	218.6	0.0209	46.0
0.139	200.8	0.0188	41.8
0.126	186.2		
0.113	172.6		
0.102	160.0		
0.0915	147.5		
0.0824	137.0		
0.0741	127.6		
0.0667	120.3		
0.06	111.9		

conc. _{tot} , mM	κ, μS/cm	conc. _{tot} , mM	κ, μS/cm
0.262	338.9	0.0355	70.1
0.236	310.7	0.0319	64.9
0.213	283.5	0.0287	58.6
0.191	258.4	0.0258	53.4
0.172	238.5	0.0233	49.2
0.155	220.7		
0.139	201.9		
0.126	186.2		
0.113	171.5		
0.102	159.0		
0.0915	147.5		
0.0824	137.0		
0.0741	126.6		
0.0667	117.2		
0.0600	108.8		
0.0540	100.4		
0.0486	92.1		
0.0438	83.7		
0.0394	76.4		

with y (CTAB) = 0.7

conc. _{tot} , mM	κ, μS/cm	conc. _{tot} , mM	κ, μS/cm
0 40	466 5	0.054	88 9
0.36	424.7	0.0486	81.6
0.324	387.0	0.0438	74.3
0.292	352.5	0.0394	66.9
0.262	321.1	0.0355	61.7
0.236	291.8	0.0319	56.5
0.213	265.7	0.0287	51.3
0.191	243.7		
0.172	223.8		
0.155	205.0		
0.139	187.2		
0.126	172.6		
0.113	159		
0.102	146.4		
0.0915	134.9		
0.0824	126.6		
0.0741	116.1		
0.0667	105.7		
0.0600	97.3		

with	y	(CTAB)	=	0.8
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conc. _{tot} , mM	κ, μS/cm	conc. _{tot} , mM	κ, μS/cm
0.810	484.3	0.101	93.1
0.729	441.4	0.0904	87.9
0.656	403.8	0.0814	80.5
0.591	370.3	0.0732	75.3
0.531	340.0	0.0660	70.1
0.478	311.7	0.0593	66.0
0.431	286.6	0.0534	60.7
0.387	263.6		
0.349	242.7		
0.314	223.8		
0.282	207.1		
0.254	191.4		
0.229	175.7		
0.206	163.2		
0.180	150.0		
0.169	141.2		
0.152	130.8		
0.137	120.3		
0.123	110.9		
0.110	100.0		

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conc. _{tot} , mM	к, µS/cm	conc. _{tot} , mM	κ, μS/cm
1.181	653.8		
1.063	594.1		
0.957	538.7		
0.861	488.5		
0.775	443.5		
0.697	402.7		
0.628	365.1		
0.565	330.5		
0.508	300.2		
0.458	273.0		
0.412	246.9		
0.371	224.9		
0.334	205.0		
0.300	186.2		
0.270	168.4		
0.243	152.7		
0.219	139.1		

conc. _{tot} , mM	к, µS/ст	conc. _{tot} , mM	κ, μS/cm
0.236	306.5	0.0319	90.0
0.213	285.6	0.0287	82.6
0.191	266.7	0.0258	75 3
0.172	251.0	0.0230	69.0
0.172	231.0	0.0252	62.0
0.155	255.4	0.0209	03.8
0.139	220.7	0.0188	58.6
0.126	209.2		
0.113	197.7		
0.102	187.2		
0.0915	176.8		
0.0824	168.4		
0.0741	159.0		
0.0667	151.7		
0.06	143.3		
0.054	134.9		
0.0486	125.5		
0.0437	117.2		
0.0394	108.8		
0.0354	99.4		

0 170 021 0	0.0222	51 1
0.172 251.2	0.0255	J4.4
0.155 216.5	0.0209	49.2
0.139 200.8		
0.126 188.3		
0.113 176.8		
0.102 168.4		
0.0915 158.0		
0.0824 149.6		
0.0741 141.2		
0.0667 133.9		
0.0600 124.5		
0.0540 117.2		
0.0486 108.8		
0.0438 99.4		
0.0394 91.0		
0.0355 82.6		
0.0319 74.3		
0.0287 66.9		
0.0258 59.6		

conc. _{tot} , mM	κ, μS/cm	conc. _{tot} , mM	κ, μS/cm
0.172	228.0	0.0233	55.4
0.155	215.5		
0.139	200.8		
0.126	186.2		
0.113	174.7		
0.102	164.2		
0.0915	154.8		
0.0824	145.4		
0.0741	137.0		
0.0667	130.8		
0.06	122.4		
0.054	115.1		
0.0486	106.7		
0.0438	99.4		
0.0394	88.9		
0.0355	81.6		
0.0319	74.3		
0.0287	66.9		
0.0258	60.7		

conc. _{tot} , mM	κ, μS/cm	conc. _{tot} , mM	κ, μS/cm
0.324	373.4	0.0394	88.9
0.292	345.2	0.0354	80.5
0.262	320.1	0.0319	73.2
0.236	298.1	0.0287	65.9
0.213	277.2	0.0258	59.6
0.191	257.3	0.0232	54.4
0.172	239.5		
0.155	223.8		
0.139	209.2		
0.126	195.6		
0.113	184.1		
0.102	172.6		
0.0915	162.1		
0.0824	152.7		
0.0741	144.4		
0.0667	134.9		
0.06	126.6		
0.054	117.2		
0.0486	107.7		
0.0437	98.3		

with y(CTAB) = 0.4

conc. _{tot} , mM	κ, μS/cm	conc. _{tot} , mM	κ, μS/cm
0.236	293 9	0.0319	65 9
0.213	267.8	0.0287	60.7
0.191	246.9	0.0258	54.4
0.172	231.2	0.0250	54.4
0.172	214.4		
0.139	198.8		
0.126	183 1		
0.120	174 7		
0.102	160.0		
0.0015	151.7		
0.0915	130.1		
0.07/1	129.7		
0.0741	123.7		
0.0007	122.4		
0.06	114.0		
0.054	103.6		
0.0486	97.3		
0.0438	86.9		
0.0394	79.5		
0.0355	72.2		

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conc. _{tot} , mM	κ, μS/cm	conc. _{tot} , mM	κ, μS/cm
0.075		0.0400	
0.365	389.1	0.0493	87.9
0.328	357.7	0.0444	79.5
0.295	331.6	0.0399	73.2
0.266	303.3	0.0359	63.8
0.239	280.3	0.0323	58.6
0.215	260.5	0.0291	52.3
0.194	239.5		
0.174	221.8		
0.157	207.1		
0.141	192.5		
0.127	178.9		
0.114	169.5		
0.103	159.0		
0.0927	147.5		
0.0834	136.0		
0.0751	127.6		
0.0676	118.2		
0.0608	108.8		
0.0547	98.3		

conc. _{tot} , mM	κ, μS/cm	conc. _{tot} , mM	κ, μS/cm
0 224	256 7	0.0429	75 2
0.324	550.7	0.0458	/5.5
0.292	330.5	0.0394	69.0
0.262	300.2	0.0355	62.8
0.236	276.1	0.0319	56.5
0.213	254.2	0.0287	51.2
0.191	233.3	0.0258	47.07
0.172	214.4		
0.155	198.7		
0.139	184.1		
0.126	174.7		
0.113	159.0		
0.102	148.5		
0.0915	138.1		
0.0824	126.6		
0.0741	120.3		
0.0667	108.8		
0.06	101.5		
0.054	91.0		
0.0486	83.7		

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with y (CTAB) = 0.7

conc. _{tot} , mM	κ, μS/cm	conc. _{tot} , mM	κ, μS/cm
0.324	373.4	0 0438	72 2
0.292	344.1	0.0394	65.9
0.262	314.9	0.0355	59.6
0.236	288.7		
0.213	264.6		
0.191	242.7		
0.172	222.8		
0.155	205.0		
0.139	188.3		
0.126	174.7		
0.113	160.0		
0.102	148.53		
0.0915	135.0		
0.0824	123.4		
0.0741	110.9		
0.0667	101.5		
0.06	92.0		
0.054	84.7		
0.0486	78.5		

with y (CTAB) = 0.8

conc. _{tot} , mM	κ, μS/cm	conc. _{tot} , mM	κ, μS/cm
0.365	392.3		
0.328	357.7		
0.295	328.4		
0.266	301.3		
0.239	275.1		
0.215	250.0		
0.194	228.0		
0.174	207.1		
0.157	189.3		
0.141	175.7		
0.127	162.1		
0.114	148.5		
0.103	136.0		
0.0927	127.6		
0.0834	114.0		
0.0751	103.6		
0.0676	95.2		
0.0608	84.7		
0.0547	77.4		

71.1

conc. _{tot} , mM	κ, μS/cm	conc. _{tot} , mM	κ, μS/cm
0.686	733.3	0.0927	116.1
0.618	662.1	0.0834	106.7
0.556	603.5	0.0751	97.3
0.5	545.0	0.0676	86.8
0.45	497.0	0.0608	78.5
0.405	451.9	0.0547	70.1
0.365	411.1	0.0493	62.8
0.328	373.4		
0.295	340.0		
0.266	306.5		
0.239	278.2		
0.215	255.2		
0.194	229.1		
0.174	208.2		
0.157	190.4		
0.141	174.7		
0.127	158.0		
0.114	142.3		
0.103	129.7		

conc. _{tot} , mM	к, µS/cm	conc. _{tot} , mM	κ, μS/cm
0.4	533.5	0.054	158.0
0.36	496.9	0.0486	144.4
0.324	465.5	0.0437	131.8
0.292	435.1	0.0394	119.2
0.262	407.9	0.0354	107.7
0.236	384.9	0.0319	97.3
0.213	361.9	0.0287	87.9
0.191	341.0	0.0258	78.5
0.172	323.2	0.0232	70.1
0.155	305.4	0.0209	62.8
0.139	288.7	0.0188	55.4
0.126	273.0		
0.113	257.3		
0.102	242.7		
0.0915	228.0		
0.0824	214.4		
0.0741	199.8		
0.0667	185.1		
0.06	171.5		

conc. _{tot} , mM	κ, μS/cm	conc. _{tot} , mM	κ, μS/cm
0.324	458.2	0.0437	129.7
0.292	427.8	0.0394	117.2
0.262	398.5	0.0354	106.7
0.236	373.4	0.0319	95.2
0.213	353.6	0.0287	85.8
0.191	334.7	0.0258	76.4
0.172	315.9	0.0232	69.0
0.155	300.2	0.0209	60.7
0.139	282.4	0.0188	54.4
0.126	268.8		
0.113	254.2		
0.102	238.5		
0.0915	225.9		
0.0824	211.3		
0.0741	197.7		
0.0667	183.1		
0.0 6	171.5		
0.054	156.9		
0.0486	143.3		

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conc. _{tot} , mM	κ, μS/cm	conc. _{tot} , mM	κ, μS/cm
496.85	482.2	144.35	136.0
465.47	447.7	131.8	123.4
435.14	418.4	119.24	113.0
407.94	395.4	107.74	101.5
384.93	368.2	97.28	90.0
361.92	347.3	87.86	82.6
341	328.4		
323.21	310.7		
305.43	292.9		
288.7	275.1		
273.01	260.5		
257.32	244.8		
242.67	231.2		
228.03	218.6		
214.43	202.9		
199.79	189.3		
185.14	174.7		
171.54	162.1		
157.95	148.5		

conc. _{tot} , mM	κ, μS/cm	conc. _{tot} , mM	κ, μS/cm
0.26	452.0	0.0427	107 7
0.30	432.9	0.0437	107.7
0.324	426.8	0.0394	96.2
0.292	394.3	0.0354	85.8
0.262	369.2	0.0319	76.4
0.236	348.3	0.0287	69.0
0.213	324.3	0.0258	61.7
0.191	308.6	0.0232	55.4
0.172	288.7		
0.155	270.9		
0.139	255.2		
0.126	240.6		
0.113	227.0		
0.102	212.3		
0.0915	198.7		
0.0824	185.1		
0.0741	170.5		
0.0667	158.0		
0.06	145.4		
0.054	130.8		
0.0486	120.3		

with y (CTAB) = 0.4

conc. _{tot} , mM	κ, μS/cm	conc. _{tot} , mM	κ, μS/cm
0.36	460.2	0.0486	115.1
0.324	423.6	0.0437	102.5
0.292	397.5	0.0394	93.1
0.262	371.3	0.0354	83.7
0.236	345.2	0.0319	75.3
0.213	322.2	0.0287	68.0
0.191	302.3		
0.172	283.5		
0.155	266.7		
0.139	250.0		
0.126	234.3		
0.113	218.6		
0.102	205.0		
0.0915	193.5		
0.0824	179.9		
0.0741	167.4		
0.0667	151.7		
0.06	138.1		
0.054	126.6		
Table 3A-(e) Conductivity of Binary System CTAB+16-6-16 2Br⁻ at 46.5 °C with y (CTAB) = 0.5

conc. _{tot} , mM	κ, μS/cm	conc. _{tot} , mM	κ, μS/cm
0.262	358.8	0.0354	72.2
0.236	333.7	0.0319	65.9
0.213	308.6	0.0287	58.6
0.191	287.7		
0.172	267.8		
0.155	250.0		
0.139	234.3		
0.126	218.6		
0.113	205.0		
0.102	191.4		
0.0915	177.8		
0.0824	164.2		
0.0741	149.6		
0.0667	138.1		
0.06	124.5		
0.054	111.9		
0.0486	102.5		
0.0437	91.0		
0.0394	81.6		

Table 3A-(e) Conductivity of Binary System CTAB+16-6-16 2Br⁻ at 46.5 °C

with y(CTAB) = 0.6

conc. _{tot} , mM	κ, μS/cm	conc. _{tot} , mM	κ, μS/cm
0.36	435.1	0.0486	94.1
0.324	403.8	0.0437	86.8
0.292	375.5	0.0394	80.5
0.262	348.3	0.0354	70.1
0.236	325.3	0.0319	63.8
0.213	303.3	0.0287	56.5
0.191	281.4		
0.172	262.6		
0.155	245.8		
0.139	227.0		
0.126	216.5		
0.113	200.8		
0.102	185.1		
0.0915	171.5		
0.0824	155.9		
0.0741	142.3		
0.0667	129.7		
0.06	118.2		
0.054	106.7		

Table 3A-(e) Conductivity of Binary System CTAB+16-6-16 2Br⁻ at 46.5 °C with y (CTAB) = 0.7

conc. _{tot} , mM	κ, μS/cm	conc. _{tot} , mM	κ, μS/cm
0 324	307 3	0.0437	73 2
0.292	360.9	0.0394	64.9
0.262	332.6	0.0354	57.5
0.236	306.5	0.0319	52.3
0.213	281.4	0.0287	47.1
0.191	262.6		
0.172	241.6		
0.155	224.9		
0.139	207.1		
0.126	196.7		
0.113	177.8		
0.102	166.3		
0.0915	147.5		
0.0824	137.0		
0.0741	121.3		
0.0667	110.9		
0.06	98.3		
0.054	90.0		
0.0486	80.5		

Table 3A-(e) Conductivity of Binary System CTAB+16-6-16 2Br⁻ at 46.5 °C

with y (CTAB)	= 0.8	3
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conc. _{tot} , mM	к, µS/cm	conc. _{tot} , mM	κ, μS/cm
04	456 1	0.0486	70 5
0.7	410.5	0.0480	13.5
0.30	419.5		
0.324	386.0		
0.292	354.6		
0.262	325.3		
0.236	299.2		
0.213	275.1		
0.191	253.1		
0.172	234.3		
0.155	216.5		
0.139	199.8		
0.126	184.1		
0.113	169.5		
0.102	154.8		
0.0915	141.2		
0.0824	129.7		
0.0741	117.2		
0.0667	106.7		
0.06	97.3		
0.054	87.9		

Table 3A-(e) Conductivity of Binary System CTAB+16-6-16 2Br⁻ at 46.5 °C with y (CTAB) = 0.9

conc. _{tot} , mM	κ, μS/cm	conc. _{tot} , mM	κ, μS/cm
0.861	869.2		
0.775	797.1		
0.697	737.4		
0.628	669.4		
0.565	616.1		
0.508	555.4		
0.458	505.2		
0.412	460.2		
0.371	422.6		
0.334	378.7		
0.300	346.2		
0.270	318.0		

with y(CTAB) = 0

conc. _{tot} , mM	κ, mS/cm	conc. _{tot} , mM	κ, mS/cm
3.00	1.44	0.405	0.447
2.70	1.36	0.365	0.402
2.43	1.28	0.328	0.365
2.19	1.20	0.295	0.328
1.97	1.14	0.266	0.297
1.77	1.08	0.239	0.268
1.59	1.02	0.215	0.242
1.44	0.973	0.194	0.219
1.29	0.927	0.174	0.198
1.16	0.886	0.157	0.178
1.05	0.849		
0.941	0.813		
0.847	0.781		
0.763	0.750		
0.686	0.716		
0.618	0.663		
0.556	0.602		
0.500	0.545		
0.450	0.493		

with y (CTAB) = 0.1

conc. _{tot} , mM	κ, mS/cm	conc. _{tot} , mM	κ, mS/cm
3.00	1.43	0.4053	0.437
2.70	1.35	0.3647	0.395
2.43	1.27	0.3283	0.358
2.19	1.20	0.2954	0.323
1.97	1.13	0.2659	0.294
1.77	1.08	0.2393	0.264
1.59	1.02	0.2154	0.239
1.44	0.966	0.1938	0.218
1.29	0.924	0.1744	0.196
1.16	0.883	0.157	0.177
1.05	0.845	0.1413	0.160
0.941	0.813		
0.847	0.779		
0.763	0.748		
0.686	0.708		
0.618	0.652		
0.556	0.592		
0.500	0.536		
0.450	0.483		

with y(CTAB) = 0.2

conc. _{tot} , mM	κ, mS/cm	conc. _{tot} , mM	κ, mS/cm
2.70	1.39	0.365	0.415
2.43	1.31	0.328	0.373
2.1	1.24	0.295	0.338
1.97	1.18	0.266	0.305
1.77	1.11	0.239	0.278
1.59	1.06	0.215	0.250
1.44	1.01	0.194	0.227
1.29	0.966	0.174	0.204
1.16	0.929	0.157	0.185
1.05	0.886	0.141	0.168
0.941	0.848		
0.847	0.815		
0.763	0.781		
0.686	0.741		
0.618	0.679		
0.556	0.614		
0.500	0.557		
0.450	0.507		
0.405	0.458		

conc. _{tot} , mM	κ, mS/cm	conc. _{tot} , mM	κ, mS/cm
1.44	1.47	0.402	0.418
1.36	1.39	0.365	0.376
1.28	1.31	0.328	0.340
1.20	1.24	0.297	0.308
1.14	1.18	0.268	0.279
1.08	1.12	0.242	0.253
1.02	1.06	0.219	0.228
0.973	1.02	0.198	0.206
0.927	0.967	0.178	0.187
0.886	0.928		
0.849	0.891		
0.813	0.855		
0.781	0.820		
0.750	0.787		
0.716	0.743		
0.663	0.679		
0.602	0.615		
0.545	0.561		
0.493	0.504		
0.447	0.458		

with y (CTAB) = 0.3

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with y (CTAB) = 0.4

conc. _{tot} , mM	κ, mS/cm	conc. _{tot} , mM	κ, mS/cm
1.44	1.46	0.447	0.431
1.36	1.38	0.402	0.388
1.28	1.30	0.365	0.348
1.20	1.23	0.328	0.315
1.14	1.17	0.297	0.285
1.08	1.11	0.268	0.256
1.02	1.06	0.242	0.231
0.973	1.01	0.219	0.207
0.927	0.963	0.198	0.187
0.886	0.922	0.178	0.170
0.849	0.883		
0.813	0.847		
0.781	0.813		
0.750	0.776		
0.716	0.719		
0.6632	0.651		
0.602	0.586		
0.545	0.531		
0.493	0.476		

with y(CTAB) = 0.5

conc. _{tot} , mM	κ, mS/cm	conc. _{tot} , mM	κ, mS/cm
2.00	1.50	0.405	0.447
3.00	1.50	0.405	0.447
2.70	1.41	0.365	0.406
2.43	1.34	0.328	0.365
2.19	1.27	0.295	0.331
1.97	1.21	0.266	0.298
1.77	1.15	0.239	0.270
1.59	1.09	0.215	0.244
i.44	1.05	0.194	0.220
1.29	1.00	0.174	0.199
1.16	0.958		
1.05	0.919		
0.941	0.882		
0.847	0.845		
0.763	0.797		
0.686	0.733		
0.618	0.665		
0.556	0.604		
0.500	0.547		
0.450	0.495		

with y (CTAB) = 0.6

conc. _{tot} , mM	κ, mS/cm	conc. _{tot} , mM	κ, mS/cm
3.00	1.49	0.405	0.431
2.70	1.40	0.365	0.389
2.43	1.32	0.328	0.353
2.19	1.26	0.295	0.318
1.97	1.19	0.266	0.288
1.77	1.14	0.239	0.261
1.59	1.08	0.215	0.234
1.44	1.03	0.194	0.212
1.29	0.993	0.174	0.193
1.16	0.950		
1.05	0.911		
0.941	0.873		
0.847	0.834		
0.763	0.779		
0.686	0.712		
0.618	0.644		
0.556	0.584		
0.500	0.529		
0.450	0.477		

with y (CTAB) = 0.7

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conc. _{tot} , mM	κ, mS/cm	conc. _{tot} , mM	κ, mS/cm
3.00	1.52	0.405	0.453
2.70	1.44	0.365	0.409
2.43	1.37	0.328	0.369
2.19	1.30	0.295	0.334
1.97	1.24	0.266	0.301
1.77	1.18	0.239	0.272
1.59	1.13	0.215	0.247
1.44	1.09	0.194	0.223
1.29	1.05		
1.16	1.00		
1.05	0.963		
0.941	0.927		
0.847	0.883		
0.763	0.820		
0.686	0.746		
0.618	0.678		
0.556	0.612		
0.500	0.552		
0.450	0.500		

with y (CTAB) = 0.8

conc. _{tot} , mM	κ, mS/cm	conc. _{tot} , mM	κ, mS/cm
3.00	1.49	0.405	0.432
2.70	1.41	0.365	0.390
2.43	1.34	0.328	0.355
2.19	1.27	0.295	0.320
1.97	1.21	0.266	0.290
1.77	1.15	0.239	0.263
1.59	1.11	0.215	0.241
1.44	1.06	0.194	0.218
1.29	1.02		
1.16	0.979		
1.05	0.942		
0.941	0.905		
0.847	0.855		
0.763	0.784		
0.686	0.710		
0.618	0.642		
0.556	0.581		
0.500	0.526		
0.450	0.476		

.

with y (CTAB) = 0.9

conc. _{tot} , mM	κ, mS/cm	conc. _{tot} , mM	κ, mS/cm
3 00	1 55	0.405	0 441
5.00	1.55	0.405	0.441
2.70	1.47	0.365	0.399
2.43	1.40	0.328	0.361
2.19	1.33	0.295	0.325
1.97	1.27	0.266	0.294
1.77	1.21	0.239	0.266
1.59	1.16	0.215	0.240
1.44	1.12		
1.29	1.07		
1.16	1.03		
1.05	0.998		
0.941	0.954		
0.847	0.887		
0.763	0.807		
0.686	0.730		
0.618	0.662		
0.556	0.598		
0.500	0.541		
0.450	0.489		

Chapter 4

Cationic Polymeric Surfactants based on Polyethyleneimine

4.1 Theory

4.1.1. Micellar-enhanced Ultrafiltration (MEUF)

Waste water streams containing dissolved heavy metal ions and organic molecules are a common environmental problem. These metal ions and organic compounds are often very toxic and must be removed before the water can be discharged to the environment or be reused. Ordinary technologies used for removing toxic heavy metal ions are ion exchange and chemical precipitation [1-3]. Chemical precipitation is performed by precipitating the metals as hydroxides with the addition of lime. However, anionic materials such as chromate ion (CrO_4^{2-}) cannot be precipitated in this process. To make the precipitation possible, the chromate anions have to be reduced to Cr^{3+} cations by ferrous sulfate or an acidic sulfide. Such kind of treatment produces a large volume of metal hydroxide sludge, and the cost is very high [2-5]. Obviously, the current technology is not industrially practical for the removal of anionic metal ions.

The techniques for removal of organic compounds from aqueous streams include distillation, or extraction followed by distillation in which a phase change is involved. These processes require a large amount of energy. Therefore, low-energy separation technique is more desirable [6]. Besides the disadvantage mentioned above, the traditional methods are also ineffective in the removal of organic compounds with molecular weights

below 300 [7].

Micellar-enhanced ultrafiltration (MEUF), as illustrated in Figure 4.1.1-1 [5-8], is an efficient method for removing metal ions and soluble, low-molecular weight organics from aqueous systems [5]. In this method, a surfactant is added to the waste water containing metal ions or organic compounds. When the surfactant is above the critical micelle





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concentration (cmc), the pollutant species can either bound to the surface of the micelles or solubilize into the micelles. The polluted water with the surfactant is then made (under a high pressure) to pass through a membrane with the molecular cut-off small enough to block most of the micelles in the retentate side. If the solubility of the metal ions or the organics in the micelle is high, the concentration of the free pollutant in the retentate side would be very small. Since the concentration of the pollutant molecules in the retentate side approximately equals the concentration of the free pollutant molecules in the retentate side, a very pure permeate could be obtained. Ideally, the permeate side will be practically pure water, containing only low concentrations of the monomeric surfactant, the unbound metal ions, and the unsolubilized organic compounds. In addition to being an effective technique, MEUF is also a low-energy cost process. After the ultrafiltration, the retentate side has a much higher concentration of pollutant and a much smaller volume than that of the original solution. Therefore, the subsequent treatment of the retentate using the conventional methods will be less expensive and requires less energy than treating the original solution.

Micellar-enhanced ultrafiltration (MEUF) has been shown to be an effective method for removing either metal ions [8] or water-soluble organic compounds from aqueous streams [5-7, 10-13]. Monomeric micelles in the aqueous solution are usually in spherical or spheroidal shapes and contain 50 to 100 surfactant molecules. Because non-polar and slightly polar organic compounds tend to solubilize inside the micelles, MEUF is an efficient method for the removal of organic contaminants from water. For example, an overall 99% rejection for 4-tert-butylphenol (TBP) from aqueous solution has been achieved by Scamehorn and co-workers [7]. Furthermore, because ions with charges opposite to those of the ionic micelles can bound to the surface of the micelles, they can

also be removed by MEUF. Even though any anion can theoretically bound to the surface of the micelles with the opposite charges, only the removal of polyvalent ions containing metal ions (e.g., chromium, iron, and cadmium) have been reported to date[8]. The study performed by Christian and co-workers has shown that the process is highly efficient in removing CrO_4^{2-} , even in the presence of sodium chloride [8].

4.1.2. Polymeric-enhanced Ultrafiltration (PEUF)

Because surfactant monomers and micelles are in rapid equilibrium, a low concentration of surfactant monomer always passes through the membrane and goes to the permeate side during equilibrium dialysis. Furthermore, under conditions which the surfactant forms small-sized micelles, the micelles can sometimes be detected in the filtrate during ultrafiltration [5]. To help solve this problem, membranes with low molecular weight cut-off are used. However, because fluxes generally decrease as the pore diameter and molecular weight cut-off decrease, this reduces the efficiency of the ultrafiltration process.

Considering the similarities between charged micelles of ionic surfactants and polyelectrolytes [14], polyelectrolytes with molecular weight ranging from 50,000 to 500,000, sometimes in combination with monomeric surfactant, have been used for polymer-enhanced ultrafiltration, PEUF [3, 5, 15-19]. The PEUF process has two major advantages. First, because polyelectrolytes do not dissociate, they can be used at very low concentrations. In contrast, in MEUF the surfactant concentration must be considerably higher than the critical micelle concentration (cmc) so that micelles are the dominant species in the monomer-micelle equilibrium. Second, polyelectrolytes do not pass through the filtration membrane, eliminating the problem of material loss. Therefore, the high efficiency can be expected even for very low concentration of pollutants. In fact, the study

by Christian and co-workers [14] indicates that the separation efficiency increases to a large limiting value as the total concentration of ions and polyelectrolytes is reduced at a constant mole ratio. In PEUF, solutions of the polyelectrolytes should have low viscosities for it to the permeation of contaminated sites and to speed up the filtration process. Polymeric surfactants have a hydrophobic core and a hydrophilic exterior; they usually have a globular or compact conformation instead of an extended conformation adopted by many polyelectrolytes. Therefore, the efficiency of ultrafiltration may be improved if a polymeric surfactant is used instead of a simple water-soluble polymer. This is the subject of the present study.

4.1.3. Poly(ethyleneimine) [PEI]

Poly(ethyleneimine) [PEI] is a highly branched, water soluble polyelectrolyte with an elliptical shape. The structure of a segment of PEI is illustrated in Figure 4.1.3-1 [20].

Figure 4.1.3-1 The structure of PEI.

The ratio of primary, secondary, and tertiary amine nitrogen in PEI is approximately 1:2:1 [20-22]. The branching of the polymer is shown below [20].



Figure 4.1.3-2 Schematic representation of branched polyethyleneimine.

The polyethylenimines constitute a large family of water-soluble polyamines of varying molecular weight and degree of modification. The amine nitrogens in PEI are more basic than ammonia. The larger the molecular weight and the more substitution of nitrogen PEI has, the more basic it becomes. Acidification of a PEI solution produces more cationic charges on the nitrogen which binds anions well. According to the experimental results by Davis and co-workers [20], only 2.5% of the nitrogens of PEI carry positive charges at pH 10, 10% of nitrogens carry positive charges at pH 7, and as much as 50% of nitrogens carry positive charges at pH 4. A number of derivatives with different side chains attached to the primary amine groups can be prepared from PEI.

4.1.4. Hexyl PEI and lauryl PEI

Modification of PEI to include long-chain alkyl groups bound to a fraction of the total nitrogen atoms of the polymer would produce a polymeric surfactant capable of binding metal ions and solubilizing organic molecules. We have prepared two different modifications of the original polymer, hexyl PEI and lauryl PEI, and examined their capabilities in binding the negatively charged chromate ion.

4.2 Experimental

4.2.1. Materials

99% Poly(ethyleneimine) (PEI), MW 10,000, was purchased from Polysciences, Inc., and was dialysed four times using dialysis membrane tubing with 6,000-8,000 MW. cutoff. Hexyl PEI and lauryl PEI were synthesized from PEI as described below.

4.2.2 Synthesis

4.2.2.1 Hexyl PEI. PEI (12 gm) was dried in a vacuum oven. Dried PEI was mixed with 6 gm of 1-bromohexane and 8 gm of diisopropylethylamine (DPEA) in 350 ml absolute ethanol. The above mixture was refluxed for 48-72 hrs. At the end of the reaction, all volatile materials were removed using a rotatory evaporator. The residue was dissolved in water and the solution was dialysed four times in deionized water. The dialysed solution was dried first in a vented hood and then in a vacuum oven. The hexyl group content of the modified polymer was determined by NMR spectroscopy. To change the final alkylated composition, different ratios between the amount of PEI and 1-bromohexane in the starting material were used. The corresponding amount of DPEA was changed accordingly to keep the ratio of 1-bromohexane and DPEA at about 1:2.

<u>4.2.2.2 Lauryl PEI (LPEI)</u>. The procedure of synthesizing lauryl PEI was basically the same as that of the hexyl PEI except that 1-bromododecane instead of 1-bromohexane was used in the starting material.

$$-(CH_2CH_2NH) + Br(CH_2)_5CH_3$$



$$-(CH_2CH_2NH)_{n} + Br(CH_2)_{11}CH_3$$





Schematically, the structures of hexyl PEI and lauryl PEI can be represented by:

$$\begin{array}{ccc} - \left(\operatorname{CH}_{2}\operatorname{CH}_{2}\operatorname{N}\right)_{\overline{n}} & - \left(\operatorname{CH}_{2}\operatorname{CH}_{2}\operatorname{N}\right)_{\overline{n}} \\ | & | \\ \left[\left(\operatorname{CH}_{2}\right)_{5}\operatorname{CH}_{3} \right]_{x} & \left[\left(\operatorname{CH}_{2}\right)_{11}\operatorname{CH}_{3} \right]_{x} \\ \end{array}$$

$$\begin{array}{c} \text{hexyl PEI} & \text{lauryl PEI} \end{array}$$

However, it should be noted that not all amine groups are alkylated, and the polymer chain is branched.

4.2.3 ¹H NMR experiments

"100%" deuterium oxide was purchase from CIL Cambridge Isotope Laboratories. A Varian XL-300 MHz NMR spectrometer was employed in the NMR study. The experiments were performed at room temperature for lower alkylated polymers and higher temperature up to 60 °C for higher alkylated polymers. The alkylated composition was calculated from the area ratio of CH₃ peak to CH₂ peaks.

4.2.4 Viscosity Measurement

An Ostwald Viscometer was used to measure the viscosity of PEI, hexyl PEI and lauryl PEI. The measurement was performed in a 25 °C water bath. The volume of the polymer solution measured was 5 ml.

4.2.5 Ultrafiltration

A Na_2CrO_4 stock solution and a polymeric surfactant stock solution were prepared first. A retentate Na_2CrO_4 sample was made by mixing the Na_2CrO_4 stock solution with the polymer stock solution according to a pre-determined molar ratio and diluted with deionized

water to 250 ml. The final concentration of the CrO_4^{2-} in the retentate sample was 1 mM. The retentate solution was then adjusted by a standardized HCl acid to the desired pH value. The sample prepared as described above was filtrated using an ultrafiltration cell.

4.2.6 UV experiments

A Shimadzu model UV-160 recording spectrophotometer was employed to detect the chromate concentrations of the permeate samples.

A calibration curve was prepared based on the following procedure: A buffer solution of pH 8 was first prepared from NaH_2PO_4 and Na_3PO_4 . A series of Na_2CrO_4 samples were prepared by dissolving Na_2CrO_4 into the above buffer solution with the final concentrations ranging from 0.0159 mM to 0.127 mM. A calibration curve of CrO_4^{2-} was then plotted based on the measured absorbance values of the CrO_4^{2-} peak at 372 nm.

Since 95% of chromate exists as CrO_4^{2-} at pH = 8, all the permeate samples from the ultrafiltration experiments were adjusted to pH 8 by the standardized NaOH solution before being analysed by the UV spectrophotometer.

4.3 Results and Discussions

4.3.1 Synthesis of hexyl PEI and lauryl PEI

PEI is a highly branched, water soluble polymer. The branched molecular structure is schematically illustrated in Figure 4.1.3-1 [23, 24]. It had been demonstrated previously that approximately 25% of the nitrogens are primary amines, 50% secondary, and 25% tertiary [23-25] in PEI. The structure of a segment of the polymer is represented in Figure 4.1.3-2. Since PEI contains a high proportion of primary amine groups, it is possible to introduce a variety of side chains by forming an amide linkage with an added R-Br reagent. hexyl PEI and lauryl PEI were synthesized based on this principle by refluxing a solution containing PEI, 1-bromododecane (or 1-bromohexane), and diisopropylethylamine in absolute ethanol, as described in the Experimental section.

<u>4.3.1.1</u> Calculation of the Percentage of Alkylation. The percentage of alkylation of hexyl PEI and lauryl PEI was calculated from the integrated NMR ¹H spectrum using equation (4.3.1-1) and (4.3.1-2):

For hexyl PEI:

[intergration area of proton in CH ₃]	- 3x	(1011)
[intergration area of proton in CH ₂]	= 4 + 10x	(4.3.1-1)
For lauryl PEI:		
[intergration area of proton in CH ₃]	3x	(4 2 1 2)
[intergration area of proton in CH ₂]	= 4 + 22x	(4.3.1-2)

where x represents the alkylated percentage of nitrogen in PEI.

Data concerning the synthesis of hexyl PEI and lauryl PEI are summarized in Table 4.3.1-1.

		Starting Materials		alkylated percentage (%)
hexyl PEI	PEI (g)	BrC ₆ H ₁₃ (g)	Ratio (mol)	
	10.0	1.65	24:1	4
	10.3	5.1	8:1	16
	10.9	10.7	4:1	36
•		· · · · · · · · · · · · · · · · · · ·		
lauryl PEI	PEI (g)	BrC ₁₂ H ₂₅ (g)	Ratio (mol)	
	11.9	8.7	8:1	20

Table 4.3.1-1 Hexyl PEI and Lauryl PEI

<u>4.3.1.2 Viscosity Measurement</u>. Viscosity is known to be an important criterion for a polymeric surfactant. Only when the polymeric surfactant has a low viscosity, a smooth, fast, and low energy ultrafiltration is possible. Therefore, the viscosities of solutions of PEI, hexyl PEI (4% and 16% alkylated) and lauryl PEI (20% alkylated) were measured relative to that of water. The measured viscosities of polymer and water are expressed in equations (4.3.1-3) and (4.3.1-4), respectively,

$$\eta = Bt\rho \tag{4.3.1-3}$$

$$\eta_{o} = Bt_{o}\rho_{o} \qquad (4.3.1-4)$$

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where η and η_o are the measured viscosity of polymer and water, respectively, B is the viscometer constant, t and t_o are the flow times of polymer solution and water in the viscometer, respectively, ρ is the density of the polymer solution, and ρ_o is the density of water. Since B is a constant for each viscometer, it can be calculated from the viscosity of water, namely $\eta_o = 0.8904$ centipoise at 25 °C. For dilute solutions, ρ can be considered to be the same as that of water without introducing appreciable error. Therefore, equations (4.3.1-3) and (4.3.1-4) can be combined to give equation (4.3.1-5):

$$\eta = (t/t_0) \eta_0$$
 (4.3.1-5)

To measure the viscosity of a polymer solution, the flow time of water was measured first. The viscosity of a polymer solution can be calculated based on equation (4.3.1-5). Four concentrations of each polymer solution were measured and four samples of each concentration were prepared. The detailed experimental data are compiled in Table 4A (1a) through Table 4A (1e) in the Appendix. The average viscosities of the polymer solution relative to that of water are summarized in Table 4.3.1-2.

The concentrations of the polymer solutions in the viscosity measurement are from two to ten times that of the polymer solutions used in the ultrafiltration experiments, which will be discussed in the next section. Even though higher concentrations of polymer solutions were used for the viscosity measurement, the viscosities of all four polymer solutions were close to that of water. The largest viscosity difference from water was found for the 64 mM lauryl PEI (20% alkylated) sample, which is 8.6% larger than water. Therefore, as far as the viscosity is concerned, PEI is a good polyelectrolyte for PEUF, and hexyl PEI and lauryl PEI appear to be good polymeric surfactants for MEUF.

Polymer	Conc. (mM)	^t ave	η (cp)
H ₂ O		4.75	0.8904
PEI	9.76 14.6 19.5 24.4	4.81 4.81 4.80 4.86	0.902 0.902 0.900 0.911
hexyl PEI (4% alkylated)	31.0 63.0 93.0 124	4.76 4.75 4.81 4.83	0.892 0.890 0.902 0.905
hexyl PEI (16% alkylated)	32.0 51.2 64.0 76.8	4.75 4.84 4.82 4.88	0.890 0.907 0.904 0.915
lauryl PEI (20% alkylated)	16.0 32.0 48.0 64.0	4.83 4.86 4.96 5.16	0.905 0.911 0.93 0.967

Table 4.3.1-2 Viscosity of H_2O and Polymer Solutions at 25 °C

4.3.2. Ultrafiltration and UV Detection of CrO_4^{2-}

<u>4.3.2.1 pH adjustment for the permeate samples</u>. In the aqueous solution, the following equilibrium reactions occur between CrO_4^{2-} , $HCrO_4^{-}$ and $Cr_2O_7^{2-}$:

$$2 \operatorname{CrO}_4^{2-} + 2 \operatorname{H}^+ = \operatorname{Cr}_2 \operatorname{O}_7^{2-} + \operatorname{H}_2 \operatorname{O}$$
(4.3.2-1)

$$CrO_4^{2-} + H^+ = HCrO_4^-$$
 (4.3.2-2)

$$2HCrO_4^- = Cr_2O_7^{2-} + H_2O$$
 (4.3.2-3)



Figure 4.3.2-1 Fraction of CrO₄²⁻ versus pH.

The amount of each species depends on the pH value. In the aqueous solution without polymer, when pH > 8, the solution contains mainly CrO_4^{2-} , and the color is yellow. When pH < 8, the amount of CrO_4^{2-} decreases and the amounts of $HCrO_4^{-}$ and $Cr_2O_7^{2-}$ increase with the decrease of the pH value, and the color of the solution turns gradually from yellow to orange. The relation between CrO_4^{2-} and pH of the solution is represented clearly by the curve shown in Figure 4.3.2-1 calculated by Tucker and Christian [25].

In the solution with PEI, hexyl PEI or lauryl PEI, however, the equilibria between the three species are also affected by the binding between the polymer and the chromate anions. Since the charge number of CrO_4^{2-} and $Cr_2O_7^{2-}$ is two and the charge number of $HCrO_4^{-}$ is only one, CrO_4^{2-} , $Cr_2O_7^{2-}$ are more likely to bind with polymer than $HCrO_4^{-}$ does. Then, equation 4.3.2-2 is shifted to the left side and equation 4.3.2-3 is shifted to the right side in the presence of the polymer. Since the ultrafiltration experiments were performed below pH value 7, both $Cr_2O_7^{2-}$, CrO_4^{2-} and a small amount of $HCrO_4^{-}$ could be bound to the polymer. The ratio between the bound species depends on the exact pH value of the solution and the structure of the polymer. In any case, the ratio is not important because our major concern is the overall binding of the total amount of all chromate species. The amount of chromate in the final permeate sample was monitored by the absorbance of CrO_4^{2-} at 372 nm. It can be seen from Figure 4.3.2-1 that the fraction of CrO_4^{2-} is about 95% at pH 8. Therefore, a pH value 8 or higher was maintained in the analysis of the permeate, so that solutions could be analyzed quantitatively.

<u>4.3.2.2 CrO₄2- calibration</u>. A calibration curve of CrO₄2- in the pH 8 buffer solution was constructed as shown in Figure 4.3.2-2.



Figure 4.3.2-2 The CrO_4^2 - calibration line.

The absorbance data are shown in Table 4A in the appendix. The interception and the slope of the curve calculated using the program installed inside the UV spectrophotometer were -0.0002 and 0.2307, respectively. The concentrations of the permeate samples in the following ultrafiltration experiments were calculated from the calibration line.

<u>4.3.2.3</u> Effect of pH on the Ultrafiltration of CrO_4^{2-} . The effect of pH on the ultrafiltration of chromate in the presence of PEI, hexyl PEI and lauryl PEI was studied. Since the binding of CrO_4^{2-} to the polymer is determined to a great extent by the amount of positive charges the nitrogen atoms carry, the pH of the solution is therefore critical to the ultrafiltration of the cationic ions. According to Davis and co-workers [26], 10% of total nitrogens in PEI carry positive charges at pH 7, and 50% of nitrogens carry positive charges at pH 4. Obviously, the lower the pH of the solution, the better binding of cationic ions to the polymer. However, a very low pH is not practical for industrial separations. A series of chromate ultrafiltrations in the presence of PEI, hexyl PEI and lauryl PEI were

then performed at varying pH in order to determine an effective working pH value.

4.3.2.3.1 pH effect on the ultrafiltration in the presence of PEI. A set of chromate ultrafiltration experiments in the presence of PEI were performed at six different pH values varied from 5.60 to 6.95. The molar ratio between chromate and EI chosen was 1:14, where EI is the ethyleneimine unit in PEI. For each 250 ml retentate solution, 9 permeate samples were collected. The first fraction was usually discarded for the experimental condition to reach a steady state. Each permeate sample weighted between 17 to 18 g. The pH of the permeate samples were adjusted to above 8 with 0.1 M NaOH. The volume of the NaOH used for adjusting the pH was between 0.03 to 0.04 ml, which was small enough to be negligible in the calculation of the permeate concentrations.

The degree of the chromate separation through the ultrafiltration is represented by the percentage rejection, which is defined by equation (4.3.2-4) [8],

Rejection (%) =
$$\begin{bmatrix} (chromate in permeate) \\ 1 - \frac{1}{(chromate in retentate)} \end{bmatrix} x (100) (4.3.2-4)$$

where "chromate in retentate" represents the concentration of the anion while the corresponding permeate sample was being collected.

Data on the concentration and the percentage rejection of the chromate ultrafiltration in the presence of PEI versus pH are compiled in Table 4A (3a) to Table 4A (3g) in the Appendix. The rejection of chromate in the presence of PEI versus retentate concentration is shown in Figure 4.3.2-3, and the percentage rejection at retentate concentration 2.0 mM

versus pH is shown in Figure 4.3.2-4.

From Figure 4.3.2-3, it was found that percentage rejection of chromate varies with its retentate concentration. Therefore, to compare the binding at different experimental conditions, a percentage rejection value at retentate concentration 2.0 mM was chosen to represent the ultrafiltration effect at each individual pH. From the plot of percentage rejection versus pH shown in Figure 4.3.2-4, an abrupt change occurs at about pH=6.5. The pH dependence is determined by a series of equilibria:

$$\begin{split} \text{PEI} + \text{H}^{+} &= (\text{PEIH})^{+} \\ (\text{PEIH})^{+} + \text{H}^{+} &= (\text{PEIH}_{2})^{2+} \\ \text{PEI} + \text{nH}^{+} &= (\text{PEIH}_{n})^{+n} \\ (\text{PEIH}_{n})^{+n} + \text{CrO}_{4}^{2-} &= (\text{PEIH}_{n} \cdot \text{CrO}_{4})^{+(n-2)} \\ (\text{PEIH}_{n} \cdot \text{CrO}_{4})^{+(n-2)} + \text{CrO}_{4}^{2-} &= (\text{PEIH}_{n} \cdot 2\text{CrO}_{4})^{+(n-4)} \\ (\text{PEIH}_{n})^{+n} + (n/2) \text{CrO}_{4}^{2-} &= [\text{PEIH}_{n} \cdot (n/2) \text{CrO}_{4}] \end{split}$$

Because of the complexity of the equilibria, we will not attempt a quantitative analysis of the percentage rejection curves. However, since Figure 4.3.2-5 indicates that at pH = 6.5, PEI is about 15% protonated. For a chromate:EI ratio of 1:14 the ratio of negative to positive charges is about 1:1. Therefore, for pH values larger than 6.5, the positive charges in the solution are less than negative charge. This may explain the fact that the percentage rejection increased rapidly with the decrease of pH when pH value is bigger than 6.5. For pH values less than 6.5, the percentage rejection was above 99%, but it increase less rapidly with the decrease of pH. As a result, 6.5 appears to be an effective and practical working pH for the ultrafiltration procedure.

4.3.2.3.2 pH effect on the ultrafiltration in the presence of hexyl PEI (16% alkylated). As discussed in section 4.3.2.3.1, the pH value of the retentate samples has a large effect on the ultrafiltration in the presence of PEI. In hexyl PEI, part of the amine nitrogens are substituted by a 6-carbon alkyl chain. To study the pH effect on the ultrafiltration of chromate in the presence of hexyl PEI, a series of experiments similar to those of PEI were performed. The experimental conditions were the same as those for PEI except that five instead of six pH values varying from 6.00 to 6.92 were chosen for hexyl PEI experiments The percentage rejection data are compiled in Table 4A (4a) through Table 4A (4e) in the Appendix. The plot of percentage rejection versus retentate concentration is shown in Figure 4.3.2-7.



Retentate concentration (mM)

Figure 4.3.2-3 Percentage rejection of chromate in PEI (1:14) solutions

versus retentate concentration.


Figure 4.3.2-4 Percentage rejection of chromate (retentate concentration 2.0 mM) in PEI (1:14) solutions.



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Figure 4.3.2-5 Percentage of nitrogens carrying positive charges at various pH.



Figure 4.3.2-6 Percentage rejection of chromate in hexyl PEI (1:14)

versus concentration.



Figure 4.3.2-7 Percentage rejection of chromate (retentate concentration 2.0 mM) in Hexyl PEI (1:14) solutions.

Comparing Figure 4.3.2-6 with Figure 4.3.2-3, and Figure 4.3.2-7 with Figure 4.3.2-4, the plots of the percentage rejection of chromate in the presence of hexyl PEI (16% alkylated) are quite similar to the plots for PEI. In other words, the ultrafiltration process did not improve much in the presence of hexyl PEI (16%). These results are not surprising, because the six-carbon chain added in the case of hexyl PEI may not be hydrophobic enough to cause a substantial change in the conformation of PEI.

4.3.2.3.3 pH effect on the ultrafiltration in the presence of lauryl PEI (20% alkylated). To study the effect of longer alkylation chain on the ultrafiltration of chromate, a set of experiments in the presence of lauryl PEI (20% alkylated) were performed. The data obtained from these experiments are compiled in Table 4A (5a) through Table 4A(5d) in the Appendix. The graph plotted based on these data are shown in Figure 4.3.2-8 and Figure 4.3.2-9.

From Figure 4.3.2-9, the percentage rejections of chromate in the presence of lauryl PEI indeed improved considerably compared to PEI and hexyl PEI. Using PEI or hexyl PEI, percentage rejections were larger than 99% only when pH values were above 6.5 or 6.8. Using lauryl PEI, however, the percentage rejection was above 99% even for the pH value of 6.9, and the percentage rejections were larger than those for PEI and hexyl PEI over the whole pH range studied. In other words, pH did not affect the ultrafiltration of chromate as much in the presence of lauryl PEI as it did in the presence of PEI or hexyl PEI. The improvement is likely the result of much longer alkyl chains in lauryl PEI, which double the length of the alkyl chains in hexyl PEI, enabling each polymer to form a hydrophobic core in the aqueous solution, just like the formation of micelles by monomeric surfactants when the surfactant concentration is above the cmc. The positive charges thus distribute on



Figure 4.3.2-8 Percentage rejection of chromate in lauryl PEI (1:14) solutions.

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Figure 4.3.2-9 Percentage rejection of chromate (retentate concentration 2.0 mM) in lauryl PEI (1:14) solutions.

the surface of the hydrophobic core, making the binding of chromate anions more favorable. Because the cmc of a polymeric surfactant is essentially zero, an electrolyte polymer with an appropriate length of the alkylation chain, such as lauryl PEI, is more advantageous in filtration experiments because they can make a much cleaner permeate solution. Even though only chromate was studied in our work, from the discussion above, it can be predicted that water-soluble organic molecule can also be filtered by lauryl PEI due to the hydrophobic core.

4.3.2.4 Effect of Molar Ratio between Chromate and Polymer. As discussed above, the pH value plays an important role in the ultrafiltration of Chromate in the presence of PEI or hexyl PEI. In PEI (1:14) solutions, the more acidic the sample, the better percentage rejection is achieved due to the increase in the positive charges carried by the nitrogen atoms in the polymer. In hexyl PEI and lauryl PEI solutions, however, it is not true. As shown in Figure 4.3.2-7 and 4.3.2-9, the best percentage rejection occurred at pH 6.5 for hexyl PEI solutions and at pH 6.8 for lauryl PEI solutions. Therefore, a pH of value at about 6.5 seems to be an effective and acceptable pH for the polymer like PEI and hexyl PEI. Even though the best percentage rejections were obtained at pH value of 6.8 in lauryl PEI solutions, generally the pH doesn't affect the percentage rejection considerably. Besides pH, the amount of the polymer is also very important in the ultrafiltration experiment. Since the positive charge on the nitrogen determines the binding of cations, and only a certain portion of the nitrogens carries positive charge, the concentration of polymer in comparison with the concentration of chromate must also be studied in the ultrafiltration process. In order to find out the relationship between the concentration of polymer and percentage rejection, ultrafiltrations with different molar ratio between the polymer and chromate were performed.

4.3.2.4.1 Molar Ratio between Chromate and PEI. Several experiments were performed in this section.

First, a set of experiments with different pH values varying from 6.07 to 6.95 were carried out at a chromate EI ratio of 1:10. The data obtained are compiled in Table 4A (6a) through 4A (6f) in the appendix. The plots of percentage rejection versus the retentate concentration and the plot of percentage rejection versus pH are shown in Figure 4.3.2-10 and Figure 4.3.2-11, respectively. From Figure 4.3.2-10, a relationship between the percentage rejection and the retentate concentration similar to that shown in Figure 4.3.2-3 was obtained, showing that the percentage rejection increased with the increase of the retentate concentration. To compare with the results of polymer solutions with chromate:EI ratio of 1:14, the percentage rejection data for retentate concentration = 2.0 mM were also used to plot the percentage rejection versus pH as shown in Figure 4.3.2-11. Comparing the two curves at different chromate:EI ratio shown in Figure 4.3.2-11, an abrupt change of percentage rejection with pH was also found around pH 6.7. A difference between the two curves is that four out of the five percentage rejections at chromate:EI ratio of 1:10 were below 99.2 % at all pH values studied, whereas the curve at chromate:EI ratio of 1:14 was all above 99.2 % at pH below 6.5. Obviously, the molar ratio between chromate and PEI had a significant effect on percentage rejection.

Another set of experiment at a fixed pH was performed with the chromate:PEI ratios at 1:5, 1:7 and 1:17. Based on the results presented in section 4.2.3.1, 6.5 appeared to be a good and acceptable pH for the ultrafiltration in the presence of PEI, and was chosen as the pH for this set of experiment. All the experimental conditions were the same as those described in section 4.3.2.1 except for the polymer concentration. The experimental data



Figure 4.3.2-10 Percentage rejection of chromate in PEI (1:10) solutions versus retentate concentration.



Figure 4.3.2-11 Percentage rejection of chromate in PEI solutions.

are compiled in Table 4A (7a) through Table 4A (7c) in the Appendix. The plot of percentage rejection versus retentate concentration is shown in Figure 4.3.2-12. The graph plotted based on percentage rejection at 2.0 mM retentate concentration versus the chromate:EI ratio is shown in Figure 4.3.2-13. In addition to the results from the three experiments performed in this section, two more points were added using the results obtained from the former experiments. One is the point which is at chromate, EI ratio of 1:14 from section 4.3.2.1. The other point is the one at the chromate:EI ratio of 1:10. The percentage rejection at 2.0 mM retentate concentration are listed in Table 4.3.2-1.

 Table 4.3.2-1
 Percentage rejection of chromate PEI solutions

[chromate]:EI	5	7	10	14	17
Rejection (%)	92.6	97.5	99.0	99.3	99.7

at [chromate]_{ret} = 2.0 mM and pH = 6.5

The graph shown in Figure 4.3.2-13 indicates that the higher the EI:chromate ratio, the better the separation was. Also, for the chromate ultrafiltration in the presence of PEI, the amount of polymer at least ten times of that of chromate was needed to obtain a minimum of 98% rejection at pH 6.5.



Figure 4.3.2-12 Percentage rejection of chromate in PEI solutions at pH = 6.5 versus the retentage concentration.



Figure 4.3.2-13 Percentage rejection of chromate in PEI solutions with retentate concentration of 2.0 mM at pH = 6.5.

4.3.2.4.2 Molar ratio between chromate and lauryl PEI (20% alkylated). From the discussion in sections 4.3.2.3.1 and 4.3.2.4.1, both the pH and the ratio between chromate and PEI affect considerably the ultrafiltration of chromate. Compared to PEI, the results presented in section 4.3.2.3.3 show that pH did not affect the chromate ultrafiltration in the presence of lauryl PEI (20%) very much as long as it was below 7. The results suggest that lauryl PEI is a better polymeric surfactant as far as pH is concerned. In this section another set of experiments of chromate ultrafiltration in the presence of lauryl PEI is described. These experiments were performed with different ratio of chromate: EI varying from 1:5 to 1:14 at the same pH. For the convenience of comparison with the results obtained with PEI, these experiments were also performed at pH 6.5. The data obtained from these experiments are compiled in Table 4A (8a) through 4A (8d) in the appendix and the percentage rejections versus EI, chromate ratio are shown in Figure 4.3.2-14. To compare with the results obtained in PEI solution, the percentage rejections in lauryl PEI at retentate concentration 2.0 mM are plotted together with those of PEI in Figure 4.3.2-15 and the results are summarized in Table 4.3.2-2, which shows that all five rejections were above 98.0 %. Compared with the results obtained with PEI which showed that rejections were above 98% only when ratios of EI:chromate were above 10, the ultrafiltration in the presence of lauryl PEI were improved much more.

Table 4.3.2-2 Percentage rejection of CrO_4^2 - in lauryl PEI at pH = 6.50 $[CrO_4^2-]_{ret} = 2.0 \text{ mM}$

[EI]:[CrO ₄ 2-]	5	6	7	10	14
Rejection (%)	98.9	99.1	99.2	99.8	9 9.9



Figure 4.3.2-14 Percentage rejection of chromate in 20% alkylated lauryl PEI at pH = 6.5.



Figure 4.3.2-15 Percentage rejection of chromate in lauryl PEI and PEI solutions with retentate concentration 2.0 mM at pH = 6.5.

Combining the results presented in sections 4.3.2.3 and 4.3.2.4, it can be concluded that lauryl PEI is a much better polymeric surfactant than PEI and lauryl PEI for chromate ultrafiltration. Since a less acidic medium and lower polymer concentration can be used for the ultrafiltration in lauryl PEI, the final retentate solution can be processed more easily, which may be advantageous in industry.

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Bibliography

- 1. D. Bhattacharyya, M. Moffitt, R. B. Grieves, Sep. Sci. Technol. 1978, 13, 449.
- C. S. Brooks, "Metal Recovery from Industrial Waste", Lewis Publishers chelsea, 1991, P. 73-76.
- 3. S. Sriratana, J. F. Scamehorn, S. Chavadej, C. Saiwan, K. J. Haller, S. D. Christian and E. E. Tucker, Sep. Sci. Tech. 1996, 31, 2493.
- N. I. Shapiro, H. Liu, J. E. Santo, D. Fruman, C. Darvin, J. Baranski, K. Mihalik, in *Chemistry in Water Reuse*, Cooper, W. J., Ed.; Ann Arbor Science, Ann Arbor, MI, 1981, vol. 1, ch. 13, p. 281.
- E. E. Tucker, S. D. Christian, J. F. Scamehorn, H. Uchiyama, G. Wen, in *Removal* of Chromate from Aqueous Streams by Ultrafiltration and Precipitation, Sabatini, D. A.; Knox, R. C., Eds.; "Transport and Remediation of Subsurface Contaminants", 1992.
- 6. Dunn JR,R. O. and J. F. Scamehorn, Sep. Sci. Technol. 1985, 20(4), 257-284.
- R. O. Dunn JR, and J. F. Scamehorn, S. D. Christian, Sep. Sci. Technol. 1987, 22(2&3), 763-789.
- S. D. Christian, S. N. Bhat, E. E. Tucker, J. F. Scamehorn, El-Sayed, D. A. AIChE J. 1988, 34, 189.
- 9. L. L. Gibbs, J. F. Scamehorn, S. D. Christian, J. Membrane Sci. 1987, 30, 67.
- G. A. Smith, S. D. Christian, E. E. Tucker, J. F. Scamehorn, in "Equilibrium Solubilization of Benzene in Micellar Systems and Micellar-Enhanced Ultrafiltration of Aqueous Solutions of Benzene" Ordered Media in Chemical Separation, Hinze, W. L.; Armstrong, D. W. eds., Am. Chem. Soc. Symp. Ser., 1987 342, 184.
- 11.S. N. Bhat, G. A. Smith, E. E. Tucker, S. D. Christian, W. Smith, and

J. F. Scamehorn, Ind. Eng. Chem. Res., 1987, 26, 1217.

- J. F. Scamehorn, and J. H. Harwell, "Surfactant-Based Treatment of Aqueous Process Streams," Surfactants in Chemical Engineering and Process Engineering, Wasan, D. T.; Shah, D. O.; Ginn, M. E. eds., Marcel Dekker, New York, 1987a, 77.
- J. F. Scamehorn, and J. H. Harwell, "An Overview of Surfactant-Based Separation Processes," *The Role of Surfactants in New and Emerging Technologies*, Rosen, ed., Marcel Dekker, New York, **1987b**, 169.
- 14. K. J. Sasaki, S. L. Burnett, S. D. Christian, E. E. Tucker, and J. F. Scamehorn, Langmuir 1989, 5, 363.
- 15. M. Tuncay, S. D. Christian, E. E. Tucker, R. W. Taylor and J. F. Scamehorn, Langmuir 1994, 10, 4688.
- 16. M. Tuncay, S. D. Christian, E. E. Tucker, R. W. Taylor and J. F. Scamehorn, Langmuir 1994, 10, 4693.
- 17. R. Zhou, V. Palmer and K. E. Geckeler, Wat. Res. 1994, 28, 1257.
- 18. A. Tabatabai, J. F. Scamehorn and S. D. Christian, J. Membr. Sci. 1995, 30, 211.
- 19. A. Tabatabai, J. F. Scamehorn and S. D. Christian, J. Membr. Sci. 1995, 100, 193.
- 20. L. E. Davis, in "Water-soluble Resins", R. L. Davidson, and M. Sitting, Ed., New York, N. Y., 1968, Reinhold, P216.
- 21. T. Takagishi, and I. M. Klotz, Biopolymers, 1979, 18, 2497-2505.
- 22. I. M. Klotz, and T. W. Johnson, *Macromolecules*, 1974, 7, 149-153.
- I. M. Klotz, and A. R. Sloniewsky, Biochem. Biophys. Res. Commun., 1968, Vol. 31, No. 3, 421.
- M. I. Klotz, G. P. Royer, and A. R. Sloniewsky, *Biochemistry*, 1969, Vol. 8, No. 12, 4752.
- 25. S. D. Christian and E. E. Tucker, unpublished data.

26. L. E. Davis, and R. D. Deanin, SPE J., 1968, Vol. 24, 59.

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Appendix

Table 4A (1a) Viscosity of water at 25° C

t ₁	ţ	t3	t ₄	tave.	η_o
4.69	4.80	4.71	4.78	4.75	0.8904

Table 4A (1b) Viscosity of PEI at 25° C

Conc (mM)	t ₁ (s)	t ₂ (s)	t3 (s)	t ₄ (s)	$t_{ave}(s)$	η (cp)
9.76	4.89	4.79	4.80	4.74	4.81	0.902
14.6	4.78	4.85	4.82	4.80	4.81	0.902
19.5	4.79	4.81	4.81	4.77	4.80	0.900
24.4	4.83	4.91	4.85	4.85	4.86	0.911

Conc (mM)	t ₁ (s)	t ₂ (s)	t3 (s)	t ₄ (s)	t _{ave} (s)	η (cp)
	31.0	4.78	4.73	4.72	4.80	4.76	0.8923
	63.0	4.73	4.72	4.80	4.74	4.75	0.8904
	93.0	4.82	4.77	4.83	4.80	4.81	0.9016
	124	4.89	4.86	4.84	4.73	4.83	0.9054

Table 4A (1c) Viscosity of hexyl PEI (4% alkylated) at 25° C

Table 4A (1d) Viscosity of Hexyl PEI (16% alkylated) at 25° C

Conc (mM)	t ₁ (s)	t ₂ (s)	t3 (s)	t ₄ (s)	$t_{ave}(s)$	η (cp)
32.0	4.76	4.71	4.74	4.80	4.75	0.8904
51.2	4.87	4.83	4.88	4.77	4.84	0.9073
64.0	4.81	4.81	4.80	4.85	4.82	0.9035
76.8	4.88	4.89	4.90	4.83	4.88	0.9148

Conc (mM)	t ₁ (s)	t ₂ (s)	t3 (s)	t ₄ (s)	t _{ave} (s)	η (cp)
16.0	4.83	4.85	4.82	4.80	4.83	0.905
32.0	4.85	4.85	4.86	4.87	4.86	0.911
48.0	4.93	4.92	4.94	5.03	4.96	0.930
64.0	5.29	5.08	5.08	5.17	5.16	0.967

Table 4A (1e)	Viscosity	of laury	PEI (20%	alkvlated) at 25° C
	viscosicy	or manyr		unyinced) at 25 C

Table 4A (2) Absorbance of CrO_4^{2-} Calibration curve at 372 nm C = K*ABS + B K = 0.2307 B = -0.0002

No.	Conc. (mM)	ABS
1	0.0159	0.070
2	0.0278	0.120
3	0.0397	0.173
4	0.0516	0.226
5	0.0635	0.278
6	0.0793	0.345
7	0.0952	0.414
8	0.111	0.482
9	0.127	0.551

Table 4A (3a)Percentage rejection of CrO_4^2 - in PEI at pH 5.60 $[CrO_4^2-]_{ret, tot} = 1.0 \text{ mM}$ $[CrO_4^2-]_{ret, tot} : [PEI]_{tot} = 1:14$

No.	Samp. Wt.	[CrO ₄ 2-]	[CrO ₄ 2-]	Rejection
	g, per	mM, <i>per</i>	mM, ret	%
1.	18.3958	0.0202	1.040	98.06
2.	19.3047	0.0118	1.130	98.96
3.	17.4660	0.0100	1.226	99.18
4.	16.8879	0.0100	1.336	99.25
5.	17.8095	0.0093	1.476	99.37
6.	19.5107	0.0093	1.668	99.44
7.	19.3452	0.0097	1.916	99.49
8.	19.2126	0.0102	0.2483	2.247
9.	18.3831	0.0107	2.694	99.60

Table 4A (3b)Percentage rejection of CrO_4^{2-} in PEI at pH 5.93 $[CrO_4^{2-}]_{ret, tot} = 1.0 \text{ mM}$ $[CrO_4^{2-}]_{ret, tot} : [PEI]_{tot} = 1:14$

No.	Samp. Wt.	[CrO ₄ 2-]	[CrO ₄ 2-]	Rejection
	g, <i>per</i>	mM, per	mM, ret	%
1.	17.2880	0.0091	1.040	99.13
2.	17.7768	0.0091	1.122	99.19
3.	18.0150	0.0106	1.220	99.13
4.	17.7318	0.0107	1.335	99.20
5.	18.0786	0.0111	1.477	99.25
6.	17.4632	0.0116	1.646	99.30
7.	17.6929	0.0123	1.862	99.34
8.	18.0821	0.0125	2.152	99.42
9.	18.0370	0.0130	2.548	99.49

Table 4A (3c)Percentage rejection of CrO_4^2 - in PEI at pH 6.30 $[CrO_4^2-]_{ret, tot} = 1.0 \text{ mM}$ $[CrO_4^2-]_{ret, tot} : [PEI]_{tot} = 1:14$

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No.	Samp. Wt.	[CrO ₄ 2-]	[CrO ₄ ²⁻]	Rejection
	g, <i>per</i>	mM, <i>per</i>	mM, ret	%
1.	17.9805	0.0130	1.047	98.76
2.	17.8330	0.0123	1.129	98.91
3.	17.3927	0.0117	1.224	99.04
4.	17.5684	0.0115	1.339	99.14
5.	17.2064	0.0120	1.474	99.19
6.	21.9927	0.0122	1.692	99.28
7.	17.3272	0.0132	1.915	99.31
8.	17.4831	0.0140	2.211	99.37
9.	17.3513	0.0160	2.609	99.39

No.	Samp. Wt.	[CrO ₄ 2-]	[CrO ₄ 2-]	Rejection
	g, <i>per</i>	mM, per	mM, ret	%
1.	17.0258	0.0138	1.047	98.68
2.	17.6837	0.0121	1.130	98.93
3.	17.5169	0.0123	1.226	99.00
4.	17.9454	0.0127	1.343	99.05
5.	17.2385	0.0129	1.480	99.13
6.	17.0203	0.0127	1.645	99.23
7.	16.8621	0.0138	1.848	99.25
8.	17.2947	0.0151	2.120	99.29
9.	17.0921	0.0167	2.479	99.33

Table 4A (3d)Percentage rejection of CrO_4^{2-} in PEI at pH 6.55 $[CrO_4^{2-}]_{ret, tot} = 1.0 \text{ mM}$ $[CrO_4^{2-}]_{ret, tot} : [PEI]_{tot} = 1:14$

No.	Samp. Wt.	[CrO ₄ 2-]	[CrO ₄ 2-]	Rejection
	g, per	mM, <i>per</i>	mM, ret	%
1.	17.5521	0.0167	1.050	98.4 1
2.	17.1585	0.0175	1.131	98.45
3.	16.9937	0.0186	1.223	98.48
4.	16.7159	0.0192	1.331	98.56
5.	17.7018	0.0188	1.468	98.72
6.	17.5781	0.0200	1.637	98.78
7.	16.3289	0.0220	1.831	98.80
8.	18.4492	0.0227	2.117	98.93
9.	17.6140	0.0239	2.489	99.04

Table 4A (3e)Percentage rejection of CrO_4^{2-} in PEI at pH 6.76 $[CrO_4^{2-}]_{ret, tot} = 1.0 \text{ mM}$ $[CrO_4^{2-}]_{ret, tot} : [PEI]_{tot} = 1:14$

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Table 4A (3f)Percentage rejection of CrO_4^2 - in PEI at pH 6.95 $[CrO_4^2-]_{ret, tot} = 1.0 \text{ mM}$ $[CrO_4^2-]_{ret, tot} : [PEI]_{tot} = 1:14$

No.	Samp. Wt.	[CrO ₄ 2-]	[CrO ₄ 2-]	Rejection
	g, <i>per</i>	mM, <i>per</i>	mM, ret	%
1.	17.8047	0.0239	1.053	97.73
2.	16.6044	0.0229	1.130	97.97
3.	17.2279	0.0240	1.224	98.04
4.	17.8512	0.0250	1.339	98.13
5.	17.2896	0.0267	1.475	98.19
б.	17.3319	0.0286	1.641	98.26
7.	17.9022	0.0300	1.857	98.38
8.	19.4127	0.0312	2.169	98.56
9.	16.9216	0.0335	2.543	98.68

 Table 4A (3g)
 Percentage Rejection of CrO₄²⁻ in PEI

 $[CrO_4^{2-}]_{ret} = 2.0 \text{ mM} \quad [CrO_4^{2-}]:[EI] = 1:14$

pН	5.60	5.93	6.30	6.55	6.76	6.9 5
Rejection, %	99.50	99.40	99.30	99.25	98.90	99.50

Table 4A (4a)Percentage rejection of CrO₄2- in hexyl PEI (16 %) at pH6.00

$$[CrO_4^{2-}]_{ret, tot} = 1.0 \text{ mM} \quad [CrO_4^{2-}]_{tot}: [EI]_{tot} = 1:14$$

No.	Samp. Wt.	[CrO ₄ 2-]	[CrO ₄ ²⁻]	Rejection
	g, <i>per</i>	mM, per	mM, ret	%
1	10 1226	0.0000	1.014	00.11
1.	18.1330	0.0090	1.014	99.11
2.	18.5011	0.0097	1.096	99.11
3.	18.3309	0.0102	1.192	99.14
4.	18.6604	0.0109	1.307	99.17
5.	18.6758	0.0117	1.448	99.19
6.	18.3694	0.0127	1.619	99.22
7.	18.2123	0.0139	1.835	99.24
8.	18.2849	0.0153	2.119	99.28
9.	18.0384	0.0170	2.500	99.32

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Table 4A (4b)	Percentage rejection of	CrO ₄ 2- in hexyl PEI (16%) at pH 6.32	
[$CrO_4^{2-}]_{ret, tot} = 1.0 \text{ mM}$	$[CrO_4^{2-}]_{tot}:[EI]_{tot} = 1:14$	

No.	Samp. Wt. g, <i>per</i>	[CrO ₄ 2-] mM, <i>per</i>	[CrO ₄ 2-] mM, <i>ret</i>	Rejection %
1.	18.4639	0.0114	1.028	98.89
2.	18.4698	0.0111	1.112	99.00
3.	18.1486	0.0116	1.209	99.04
4.	17.9832	0.0109	1.323	99.18
5.	17.7186	0.0137	1.459	99.06
6.	17.9213	0.0114	1.629	99.30
7.	17.8519	0.0149	1.843	9 9.19
8.	17.5799	0.0161	2.116	99.24
9.	18.1594	0.0195	2.501	99.22

Table 4A (4c)	Percentage rejecti	on of CrO ₄ 2- in hexyl PEI at pH 6.56
[Ci	$[O_4^{2-}]_{tot} = 1.0 \text{ mM}$	$[CrO_4^{2-}]_{tot}:[EI]_{tot} = 1:14$

No.	Samp. Wt.	[CrO ₄ 2-]	[CrO ₄ 2-]	Rejection
	g, per	mM, <i>per</i>	mM, ret	%
1.	18.3947	0.0082	1.038	99.21
2.	18.0529	0.0089	1.121	99.21
3.	17.9165	0.0102	1.219	99.16
4.	17.7227	0.0100	1.333	99.25
5.	18.2857	0.0102	1.477	99.31
6.	17.9620	0.0103	1.651	99.38
7	18.7746	0.0108	1.871	99.42
8.	18.2182	0.0115	2.166	99.47
9.	18.2938	0.0126	2.573	99.51

No.	Samp. Wt.	[CrO ₄ 2-]	[CrO ₄ 2-]	Rejection
	g, <i>per</i>	mM, <i>per</i>	mM, ret	%
1.	17.5192	0.0162	1.045	98.45
2.	18.3441	0.0157	1.131	98.61
3.	17.6201	0.0165	1.228	98.66
4.	18.2429	0.0167	1.347	98.76
5.	18.2774	0.0171	1.493	98.85
6.	18.0898	0.0175	1.674	98.95
7.	17.5827	0.0184	1.897	99.03
8.	18.5410	0.0191	2.206	99.13
9.	18.1170	0.0209	2.626	99.20

Table 4A (4d)Percentage rejection of CrO_4^2 - in hexyl PEI (16%) at pH 6.78 $[CrO_4^2-]_{ret, tot} = 1.0 \text{ mM}$ $[CrO_4^2-]_{ret, tot} : [EI]_{tot} = 1:14$

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No.	Samp. Wt.	[CrO ₄ 2-]	[CrO ₄ 2-]	Rejection
	g, per	mM, per	mM, ret	%
1.	18.8920	0.0336	1.050	96.80
2.	18.9786	0.0275	1.139	97.60
3.	18.1903	0.0235	1.240	98.10
4.	18.1807	0.0204	1.361	98.50
5.	18.0070	0.0196	1.509	98 .70
6.	19.5636	0.0223	1.710	98.70
7.	17.6780	0.0229	1.946	98.80
8.	17.9584	0.0251	2.261	98.90
9.	18.5212	0.0283	2.720	99.00

Table 4A (4e)Percentage rejection of CrO_4^2 - in hexyl PEI (16%) at pH 6.92 $[CrO_4^2-]_{ret, tot} = 1.0 \text{ mM}$ $[CrO_4^2-]_{ret, tot} : [EI]_{tot} = 1:14$

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Table 4A (5a)Percentage rejection of CrO_4^2 - in LPEI at pH 6.95 $[CrO_4^2-]_{ret, tot} = 1.0 \text{ mM}$ $[CrO_4^2-]_{ret, tot} : [EI]_{tot} = 1:14$

No.	Samp. Wt.	[CrO ₄ 2-]	[CrO ₄ 2-]	Rejection
	g, per	mM, per	mM, ret	%
1.	17. 40 44	0.0056	1.056	99.47
2.	18.1512	0.007	1.143	99.39
3.	18.0763	0.0078	1.245	99.37
4.	17.7636	0.0082	1.366	99.40
5.	18.2416	0.0096	1.516	99 .37
6.	17.7851	0.0089	1.699	99.48
7.	17.9781	0.0107	1.935	99.45
8.	18.8439	0.0126	2.263	99.44
9.	17.8744	0.0122	2.701	99.55
Table 4A (5b)Rejection of CrO_4^{2-} in lauryl PEI at pH 6.80 $[CrO_4^{2-}]_{ret, tot} = 1.0 \text{ mM}$ $[CrO_4^{2-}]_{ret, tot} : [EI]_{tot} = 1:14$

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No.	Samp. Wt.	[CrO ₄ 2-]	[CrO ₄ 2-]	Rejection
	g, <i>per</i>	mM, <i>per</i>	mM, ret	%
1.	17.8222	0.0037	1.051	99.65
2.	19.7601	0.0013	1.147	99.89
3.	17.8879	0.0014	1.250	99.89
4.	17.7985	0.0015	1.372	99.89
5.	17.9703	0.0016	1.520	99.89
6.	17.6880	0.0020	1.704	99.88
7.	18.0449	0.0022	1.944	99.89
8.	17.8045	0.0027	2.256	99.88
9.	18.2778	0.0036	2.701	99.87

Table 4A (5c)Percentage rejection of CrO_4^2 - in lauryl PEI at pH 6.54 $[CrO_4^2-]_{ret, tot} = 1.0 \text{ mM}$ $[CrO_4^2-]_{ret, tot} : [EI]_{tot} = 1:14$

No.	Samp. Wt.	[CrO ₄ 2-]	[CrO ₄ 2-]	Rejection
	g, per	mM, <i>per</i>	mM, ret	%
1.	17.9982	0.0056	1.039	99.46
2.	17.3981	0.0023	1.120	99.79
3.	18.0288	0.0022	1.218	9 9 .82
4.	17.9234	0.0023	1.334	99.83
5.	17.1457	0.0027	1.469	99.8 2
6.	17.8384	0.0027	1.641	99.84
7.	17.1736	0.0031	1.849	99.83
8.	17.6077	0.0035	2.126	99.84
9.	18.2615	0.0042	2.518	99.83

Table 4A (5d)Percentage rejection of CrO_4^{2-} in lauryl PEI at pH 6.07 $[CrO_4^{2-}]_{ret, tot} = 1.0 \text{ mM}$ $[CrO_4^{2-}]_{ret, tot} : [EI]_{tot} = 1:14$

No.	Samp. Wt.	[CrO ₄ 2-]	[CrO ₄ 2-]	Rejection
	g, per	mM, <i>per</i>	mM, ret	%
1.	17.2995	0.0307	1.0209	97.00
2.	17.2515	0.0082	1.0978	99.25
3.	20.3230	0.0040	1.2050	99.67
4.	17.2133	0.0036	1.3143	99.73
5.	19.5481	0.0035	1.4644	99.76
6.	16.1598	0.0040	1.6186	99.75
7.	21.4081	0.0046	1.8792	99.76
8.	17.4789	0.0051	2.1643	99.76
9.	17.0755	0.0062	2.5414	99.76

Table 4A (6a)Percentage rejection of CrO_4^2 - in PEI at pH 6.95 $[CrO_4^2-]_{ret, tot} = 1.0 \text{ mM}$ $[CrO_4^2-]_{ret, tot} : [PEI]_{tot} = 1:10$

No.	Samp. Wt.	[CrO ₄ 2-]	[CrO ₄ 2-]	Rejection
	g, <i>per</i>	mM, <i>per</i>	mM, ret	%
1.	17.1988	0.0566	1.047	94.59
2.	17.7405	0.0391	1.128	96.53
3.	17.7326	0.0408	1.223	96.66
4.	17.3490	0.0389	1.335	97.09
5.	18.2276	0.0363	1.477	97.54
6.	18.0209	0.035	1.651	97.88
7.	17.8308	0.0376	1.872	97. 99
8.	18.1289	0.0385	2.166	98.22
9.	17.8017	0.0402	2.564	98.43

No.	Samp. Wt.	[CrO ₄ 2-]	[CrO ₄ 2-]	Rejection
	g, per	mM, <i>per</i>	mM, ret	%
1.	17.6698	0.0196	1.051	98.14
2.	17.6086	0.0202	1.134	98.22
3.	17.6690	0.0212	1.231	98.28
4.	17.7571	0.0226	1.348	98.32
5.	17.3497	0.0244	1.485	98.36
6.	17.8855	0.0266	1.660	9 8.40
7.	17.6941	0.0287	1.879	98.47
8.	17.6345	0.0312	2.165	98.56
9.	17.7408	0.0347	2.559	98.64

Table 4A(6b)Percentage rejection of CrO_4^2 - in PEI at pH 6.86 $[CrO_4^2-]_{ret, tot} = 1.0 \text{ mM}$ $[CrO_4^2-]_{ret, tot} : [PEI]_{tot} = 1:10$

Table 4A (6c)Percentage rejection of CrO_4^{2-} in PEI at pH 6.73 $[CrO_4^{2-}]_{ret, tot} = 1.0 \text{ mM}$ $[CrO_4^{2-}]_{ret, tot} : [PEI]_{tot} = 1:10$

No.	Samp. Wt.	[CrO ₄ 2-]	[CrO ₄ 2-]	Rejection
	g, <i>per</i>	mM, per	mM, ret	%
1.	17.7389	0.0134	1.053	98.73
2.	17.7044	0.0150	1.136	98.68
3.	17.4290	0.0166	1.233	98.65
4.	18.0191	0.0180	1.352	98.67
5.	17.9305	0.0194	1.495	98.70
6.	17.9140	0.0212	1.674	98.73
7.	17.8160	0.0226	1.900	98.81
8.	17.7064	0.0251	2.194	98.86
9.	17.5781	0.0286	2.592	98.90

Table 4A (6d)Percentage rejection of CrO_4^{2-} in PEI at pH 6.40 $[CrO_4^{2-}]_{ret, tot} = 1.0 \text{ mM}$ $[CrO_4^{2-}]_{ret, tot} : [PEI]_{tot} = 1:10$

No.	Samp. Wt.	[CrO ₄ 2-]	[CrO ₄ 2-]	Rejection
	g, per	mM, <i>per</i>	mM, ret	%
1.	18.0613	0.0157	1.051	98.51
2.	17.2649	0.0164	1.132	98.55
3.	18.2888	0.0169	1.233	98.63
4.	18.1692	0.0169	1.354	98.75
5.	17.8084	0.0178	1.497	98.81
6.	17.3902	0.0192	1.670	98.85
7.	18.2264	0.0208	1.900	98.91
8.	18.2536	0.0229	2.207	98.96
9.	18.2548	0.0265	2.629	98.99

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Table 4A (6e)Percentage rejection of CrO_4^{2-} in PEI at pH 6.07 $[CrO_4^{2-}]_{ret, tot} = 1.0 \text{ mM}$ $[CrO_4^{2-}]_{ret, tot} : [PEI]_{tot} = 1:10$

No.	Samp. Wt.	[CrO ₄ 2-]	[CrO ₄ 2-]	Rejection
	g, <i>per</i>	mM, <i>per</i>	mM, ret	%
1.	17.6823	0.0117	1.046	98.88
2.	17.5938	0.0116	1.128	98.97
3.	17.5257	0.0127	1.224	98.96
4.	17.6790	0.0131	1.339	99.02
5.	17.7071	0.0143	1.478	99.03
6.	17.8526	0.0161	1.651	99.02
7.	17.8046	0.0169	1.870	99.10
8.	18.2000	0.0195	2.163	99.10
9.	17.9824	0.0224	2.562	99.13

 Table 4A (6f)
 Percentage rejection of CrO₄²⁻ in PEI

 $[CrO_4^{2-}]_{ret} = 2.0 \text{ mM} \quad [CrO_4^{2-}]_{tot} : [EI]_{tot} = 1:10$

pН	6.07	6.40	6.73	6.86	6.95
Rejection, %	99.1	98.9	98.8	98.5	98.1

Table 4A (7a) Rejection of CrO_4^2 - in PEI with [PEI]:[CrO_4^2 -] = 5 [CrO_4^2 -]_{tot} = 1.0 mM pH = 6.55

No.	Samp. Wt.	[CrO ₄ 2-]	[CrO ₄ 2-]	Rejection
	g, per	mM, <i>per</i>	mM, ret	%
1.	17.4263	0.1062	1.049	89.88
2.	18.0610	0.1068	1.126	90.52
3.	17.6000	0.1137	1.215	90.64
4.	17.2438	0.1164	1.318	91.17
5.	17.3459	0.1209	1.444	91.63
6.	17.7508	0.1251	1.603	92.20
7.	17.6512	0.1310	1.804	92.74
8.	17.2381	0.1390	2.051	93.22
9.	17.3953	0.1494	2.401	93.78

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Table 4A (7b) Percentage rejection of CrO_4^2 - in PEI with [PEI]:[CrO_4^2 -] = 7 [CrO_4^2 -]_{tot} = 1.0 mM pH = 6.55

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No.	Samp. Wt.	[CrO ₄ 2-]	[CrO ₄ 2-]	Rejection
	g, per	mM, per	mM, ret	%
1.	17.3772	0.0319	1.051	96.96
2.	17.9370	0.0338	1.133	97.02
3.	18.3611	0.0364	1.234	97.05
4.	17.8677	0.0394	1.350	97.08
5.	18.1103	0.0417	1.4 94	97.21
6.	17.4122	0.0456	1.665	97.26
7.	17.4943	0.0483	1.882	97.43
8.	17.6017	0.0518	2.169	97.61
9.	17.6441	0.0575	2.559	97.75

Table 4A (7c) Percentage rejection of CrO_4^2 - in PEI with [EI]:[CrO_4^2 -] = 17 [CrO_4^2 -]_{tot} = 1.0 mM pH = 6.55

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No.	Samp. Wt.	[CrO ₄ 2-]	[CrO ₄ 2-]	Rejection
	g, <i>per</i>	mM, <i>per</i>	mM, ret	%
1.	17.8022	0.0034	1.025	99.67
2.	17.1090	0.0040	1.104	99.64
3.	17.6622	0.0038	1.198	99.68
4.	18.1589	0.0038	1.311	99.71
5.	18.1414	0.0046	1.449	99.68
6.	17.8801	0.0050	1.618	99.69
7.	17.4316	0.0058	1.822	99.68
8.	18.2112	0.0063	2.101	99.70
9.	17.9579	0.0076	2.475	99.69

Table 4A (8a) Percentage rejection of CrO₄2- in lauryl PEI with [EI]:[CrO₄2-] = 5

 $[CrO_4^{2-}]_{tot} = 1.0 \text{ mM} \text{ pH} = 6.50$

No.	Samp. Wt.	[CrO ₄ 2-]	[CrO ₄ 2-]	Rejection
	g, <i>per</i>	mM, <i>per</i>	mM, ret	%
1.	17.7531	0.0231	1.052	97.80
2.	18.3880	0.0184	1.139	98.38
3.	17.7265	0.0197	1.238	98.41
4.	18.2136	0.0200	1.359	98.53
5.	18.6828	0.0197	1.512	98.70
6.	17.9040	0.0208	1.694	98.77
7.	18.1785	0.0218	1.930	98.87
8.	18.1949	0.0235	2.245	98.95
9.	18.2413	0.0254	2.688	99.06

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Table 4A (8b) Percentage rejection of CrO_4^{2-} in lauryl PEI with [EI]:[CrO_4^{2-}] = 6 [CrO_4^{2-}]_{tot} = 1.0 mM pH = 6.50

No.	Samp. Wt.	[CrO ₄ 2-]	[CrO ₄ 2-]	Rejection
	g, <i>per</i>	mM, <i>per</i>	mM, ret	%
1.	17.8434	0.0623	1.047	94.05
2.	17.7693	0.0403	1.128	96.43
3.	17.3979	0.0322	1.222	97.36
4.	18.1328	0.0238	1.340	98.22
5.	18.1642	0.0191	1.484	98.71
6.	19.2335	0.0184	1.676	98.90
7.	18.4206	0.0186	1.914	99.03
8.	18.3378	0.0178	2.228	99.20
9.	17.7485	0.0188	2.651	99.29

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Table 4A (8c) Percentage rejection of CrO_4^2 - in lauryl PEI with [EI]:[CrO_4^2 -] = 7 [CrO_4^2 -]_{tot} = 1.0 mM pH = 6.50

No.	Samp. Wt.	[CrO ₄ 2-]	[CrO ₄ 2-]	Rejection
	g, per	mM, <i>per</i>	mM, ret	%
1.	18.0600	0.0244	1.049	97.67
2.	18.0844	0.0179	1.134	98.42
3.	17.6989	0.0153	1.231	98.76
4.	17.8205	0.0139	1.349	98.97
5.	17.7714	0.0139	1.492	99.07
6.	18.0847	0.0140	1.671	99.16
7.	19.3341	0.0147	1.920	99.23
8.	18.5749	0.0149	2.240	99.33
9.	18.5102	0.0161	2.686	99.40

Table 4A (8d) Percentage rejection of CrO_4^2 - in lauryl PEI with [EI]:[CrO_4^2 -] = 10

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 $[CrO_4^{2-}]_{tot} = 1.0 \text{ mM} \text{ pH} = 6.50$

No.	Samp. Wt.	[CrO ₄ 2-]	[CrO ₄ ²⁻]	Rejection
	g, <i>per</i>	mM, <i>per</i>	mM, ret	%
1.	18.2520	0.0056	1.047	99.47
2.	18.5274	0.0053	1.134	99.53
3.	18.2694	0.0051	1.234	99.59
4.	18.1364	0.0052	1.358	99.62
5.	18.3970	0.0045	1.508	99 .70
6.	18.7161	0.0050	1.700	99.71
7.	19.0603	0.0050	1.954	99.74
8.	18.6907	0.0058	2.286	99.75
9.	19.2032	0.0061	2.796	99 .78