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MEASURING MONOMER-MICELLE EQUILIBRIUM BY USING SEMI-EQUILIBRIUM DIALYSIS

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MEASURING MONOMER-MICELLE EQUILIBRIUM
BY USING SEMI-EQUILIBRIUM DIALYSIS

A DISSERTATION APPROVED FOR THE
SCHOOL OF CHEMICAL, BIOLOGICAL AND MATERIALS ENGINEERING

BY

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ABSTRACT

Monomer-micelle equilibrium, the distribution of surfactant species between the monomer and the micelles in solution, dictates many important physical properties of surfactants. Although monomer-micelle equilibrium compositions have been experimentally determined by different methods, there are severe limitations for these experimental measurements (e.g., expensive, difficult to interpret the data, and only applicable to specific systems). The goal of this work is to develop a universal, inexpensive, user-friendly technique to measure monomer-micelle equilibrium. The suitable conditions (e.g., initial total surfactant concentration and electrolyte concentration) to use this technique are determined by the experiments with three single surfactant systems including both ionic and nonionic surfactants. After that, this technique is validated on two model binary surfactant mixtures, SDS/NP(EO)$_{10}$ and CPC/NP(EO)$_{10}$, at different surfactant ratios and three different temperatures. The results demonstrate that the kinetic data are necessary to accurately determine the surfactant monomer and micelle compositions from the SED technique. The values of CMC obtained from the SED technique show good correlation with the data from surface tension measurement and predictions from RST. This is very crucial condition for validity of the SED technique. Although the RST describes the CMC data well, the predictions of monomer and micelle compositions from RST can be in gross error when compared to the experimental data from SED technique. In some cases, the SED technique measures a CPC-rich micelle while the RST predicts a NP(EO)$_{10}$-rich micelle. The SED results at different temperatures also yield enough data to calculate

the thermodynamics properties of these studied systems. A calculation of H^E, S^E and G^E values from SED data show that the H^E and S^E values from RST significantly deviate from the values calculated from experiment data while the values of G^E from both SED technique and the RST agree well.

CHAPTER 1

1. Introduction

This dissertation can be divided into three major parts. Chapter 2 is the use of semi-equilibrium dialysis (SED) technique on three different single surfactant system, sodium dodecyl sulfate (SDS), cetylpyridinium chloride (CPC), and nonylphenol polyethoxylate with an average degree of polymerization of 10 ($NP(EO)_{10}$), to study the effect of initial retentate surfactant concentration for a cationic surfactant, the effect of electrolyte concentration for an anionic surfactant and the effect of use of nonionic surfactant. In Chapter 3, The SED technique is used to measure the mixed CMC and the monomer-micelle equilibrium compositions of two binary anionic/nonionic surfactant mixtures, $SDS/NP(EO)_{10}$ and $CPC/NP(EO)_{10}$, at 30^oC and different surfactant ratios. The experimental results are compared to the results from the surface tension measurement and the predictions from the RST. The SED experiments are conducted at 40^oC and 50^oC for $SDS/NP(EO)_{10}$ and $CPC/NP(EO)_{10}$ at different surfactant ratios to measure the mixed CMC and monomer-micelle compositions in Chapter 4. The thermodynamic values are also calculated based on the experimental data from SED technique. These calculated values are also compared to the RST predictions.

CHAPTER 2

Measuring Monomer-Micelle Equilibrium by Using Semi-Equilibrium Dialysis. I. Single Surfactant Systems

The semi-equilibrium dialysis (SED) technique is utilized in this series of three papers as a new experimental method to measure monomer-micelle equilibrium for multicomponent surfactant systems. In this Part I, the validity of the technique is demonstrated for single surfactants. At a suitable contact time between a surfactant solution in the retentate compartment of a dialysis cell and water or electrolyte solution in the permeate compartment of the cell, the permeate solution has the same concentration of surfactant as the monomer in the retentate side. At longer contact times, micelles can form in the permeate compartment. The permeate concentration of each surfactant is interpolated from kinetic data to a time at which the retentate monomer concentration is attained (equilibration time). Permeate surfactant concentration was measured as a function of time for single cationic, anionic, and nonionic surfactant systems. A simple linear interpolation of concentration vs. time both before and after the equilibration time is shown to accurately yield monomer concentrations as confirmed by comparison to CMC values. As retentate surfactant concentration increases, the equilibration time decreases. At higher retentate surfactant concentrations or with added NaCl (for ionic surfactants), the change in permeate

surfactant concentration above the CMC with time is lower, leading to more accurate interpolations.

2.1 INTRODUCTION

Monomer-micelle equilibrium is the distribution of surfactant species between the monomer and the micelles in solution. For single surfactant systems, the monomer surfactant concentration is known as the critical micelle concentration (CMC). For multicomponent systems of surfactants, the total monomer concentration is called the mixed CMC of the system and one important feature is the difference in the micellar composition as compared to the monomer. In general, monomer-micelle equilibrium is an important key to understanding and controlling many important surfactant phenomena – for example, surfactant adsorption and precipitation which are both related solely to the monomer surfactant concentrations. Therefore, the ability to measure or predict monomer-micelle composition is crucial in optimizing performance of surfactant systems in many products (e.g., laundry detergents).

Although experimental measurements of monomer-micelle equilibrium have been carried out using various techniques – for example, ultrafiltration[1-7], conductivity and ion-specific electrodes[8-25], surfactant specific electrodes[26-29], fluorescence probes[30], light scattering[31-45], small-angle neutron scattering[46-55], nuclear magnetic resonance[56-75], neutron reflection[55,76-79], and ultracentrifugation[80-83] – there are severe limitations to these techniques. The equipment involved in most of the above mentioned techniques is expensive (e.g. neutron scattering) and the results are typically difficult to interpret (e.g. ultrafiltration); or only applicable to specific systems (e.g. electrode techniques only apply to ionic surfactants). Consequently, there is no convenient, inexpensive, universally applicable method to experimentally measure the monomer-micelle equilibrium.

The semi-equilibrium dialysis (SED) technique has been developed by our laboratory to measure solubilization of organic solutes in micelles at variable solute concentrations[84-91]. The SED method is applied here to measure monomer-micelle equilibrium. The retentate compartment of a dialysis cell shown in Fig. 2.1 is initially loaded with a surfactant solution above the CMC. The permeate side is initially loaded with water or water with the same added electrolyte (e.g. NaCl) concentration as contained in the retentate. The pore size of the dialysis membrane (nominally 6KD molecular weight cut-off) is small enough to block the passage of micelles from retentate to permeate, but large enough to permit surfactant monomer to pass through. Ideally, the surfactant concentration in the permeate will plateau at a concentration corresponding to the monomer retentate concentration before rising again as micelles begin to form in the permeate. Such a window of opportunity has been observed during analysis of solubilization when solute concentration in the permeate equals unsolubilized solute concentration in the retentate although small correction factors were developed for solubilization in micelles formed on the retentate side[84,92]. While in principle, application of SED to analysis of monomer-micelle equilibrium could also yield a similar window of opportunity during which permeate samples would yield retentate monomer concentrations, we will see that sampling must be done continuously over a period of time and interpolation rules developed to determine equilibrium monomer concentrations. Since the resulting SED technique uses commonly-available inexpensive dialysis cells, many systems can be investigated simultaneously. The only analytical technique required is one capable of measuring the concentration of each surfactant in a mixture: HPLC or multiple wave length UV are example of analytical tools, depending on surfactant structure. The SED technique can

be applied to any type of surfactant and to a mixture of surfactants of any degree of complexity as long as the concentration of each component can be measured.

In this paper, we investigate the kinetics of the permeate concentration for single surfactant anionic, cationic, and nonionic surfactant systems. In Part II, we analyze two binary surfactant systems and compare observed monomer compositions to those predicted by regular solution theory (RST), the dominant model used to describe the thermodynamics of non-ideal mixing in micelles. In Part III, we use the temperature dependence of SED results to examine enthalpy and entropy contributions to nonideality of mixed micelle formation.

2.2 EXPERIMENTAL SECTION

2.2.1 Materials

High purity (99+%) cetylpyridinium chloride (CPC), obtained from Zeeland Chemicals (Zeeland, MI), was used as received. Sodium dodecyl sulfate (SDS) from Fisher Scientific (Fair Lawn, NJ) initially at 99% purity was further purified by recrystallization from water and then from methanol, followed by drying under vacuum condition at room temperature[93]. The nonionic surfactant used in this study was nonylphenol polyethoxylate with an average degree of polymerization of 10 ($NP(EO)_{10}$). This polydisperse nonionic surfactant (trade name Igepal CO-660 from Rhodia, Georgia) was used without further purification. Sodium chloride (NaCl) was Fisher Certified A.C.S. grade (Fisher Scientific, Fair Lawn, NJ).

2.2.2 Methods

Surface tension measurements using the Wilhelmy plate technique were conducted by Kruss Processor Tensiometer K12 (Kruss USA, North Carolina). The solution was placed in a crystallizing dish surrounded by a water jacket to control the temperature at 30^{o}C. Prior to the measurement, surfactant solutions were prepared and kept at 30^{o}C in a controlled temperature water bath overnight. All surfactant solutions in this study were isotropic; no precipitation, liquid crystal, coacervate, or separation of surfactant into other phases was observed.

The dialysis cells (Fig. 2.1) used in this study were made from acrylic with an approximate dimension of 3 inches by 4 inches by ½ inch thickness. On each side of the compartment, there was a chamber with an approximate volume of 7 mL. Regenerated cellulose acetate membranes with 6000 Dalton molecular weight cutoff (pore size diameter of 25-50 Å) were soaked in the retentate surfactant solution for 7 days at 30^{o}C prior to use. The soaking surfactant solution was changed to a new solution every two days. The membrane pretreatment was conducted to minimize the surfactant loss by adsorption onto the membrane during the dialysis experiment. Then, the presoaked membrane was mounted between two SED cell compartments. A known volume of a surfactant solution was placed in the retentate compartment using a 10 mL syringe. The deionized water or electrolyte solution was then injected into the permeate compartment by another 10 mL syringe. The volumes of solution in both compartments were controlled by the syringes to assure that they were the same at the beginning of experiments. After that, the SED cell was sealed in the plastic package to minimize the evaporation of the solutions inside the cell. Then, the packed SED cell was equilibrated in the incubator (Isotemp 625D, Fisher Scientific) at 30^{o}C. Each

experiment was conducted with three separate SED cells for triplicate data. After a specified contact time, both retentate and permeate solutions were drawn out from the cell and the volume measured to obtain the volume change caused by osmotic pressure. For both retentate and permeate solutions, concentrations of the CPC and $NP(EO)_{10}$ were determined by a Hewlett-Packard 8452A diode array spectrophotometer while concentrations of SDS was determined by a Dionex LC20 Chromatography System with conductivity detector.

2.3 RESULTS AND DISCUSSION

2.3.1 CMC Determination from Surface Tension

Surface tension of surfactant solutions were measured and plotted as a function of surfactant concentration. The point where there is a sharp change in surface tension is the CMC of the surfactant or surfactant mixture[94]. Table 2.1 summarizes the CMC values of all studied single surfactant systems from surface tension – the resulting values are consistent with literature values[95]. The CMC of SDS and CPC decreases as added NaCl concentration increases consistent with the Corrin-Harkins equation[96], yielding a fractional counterion binding of 0.62 and 0.61 for SDS and CPC, respectively, from the best fit for the different salinities, a very typical value[9].

2.3.2 Effect of Initial Retentate Surfactant Concentration for a Cationic Surfactant

The SED experiments were preformed to evaluate an effect of initial retentate CPC concentration on the permeate CPC concentration at 30^{o}C with no added

electrolyte. Initial retentate concentrations of CPC were $1x10^{-2}$ M, $2x10^{-2}$ M, and $2.5x10^{-1}$ M, which are 10, 20 and 250 times the CMC of this surfactant, were evaluated. Deionized water was initially in the permeate compartment of SED cells in this study. Figs. 2.2 through 2.4 show the permeate CPC concentration as a function of time for these varying initial CPC retentate concentrations. These kinetic results show that the CPC concentration in the permeate compartment dramatically increases with time at the beginning of the experiment, followed by a period of time with a reduced rate of increase in the permeate CPC concentration. The surfactant monomer is dilute enough (< about 10 mM for all surfactants studied here) to obey Henry's Law: the partial fugacity or activity of the monomer is proportional to concentration. The pseudo-phase separation model assumes that the monomer concentration remains constant at the CMC as the total surfactant concentration increases above the CMC. However, careful measurements show that the activity (ion-pair activity for ionic surfactants) increases slightly with increasing total surfactant concentration above the CMC for a single surfactant[97,98]. So, when the permeate surfactant concentration reaches the CMC, there is a small driving force for additional surfactant monomer to diffuse across the membrane. Upon reaching the permeate, this surfactant above the CMC forms micelles, so the total permeate surfactant concentration increases slowly with time above the CMC. From Figs. 2.2-2.4, there is a dramatic decrease in slope of permeate surfactant concentration vs. time at around the CMC. Although much more sophisticated mathematical techniques could be used to model these curves, we propose that the intersection of two straight lines, one below the CMC and one at concentrations modestly above the CMC, will yield the monomer concentration on the retentate side (CMC for a single surfactant) and the equilibration time required to attain it. The use

of linear interpolation procedures is simple and consistent with a user-friendly analytical technique in that interpretation of the experimental data does not require sophisticated software.

From Figs. 2.2-2.4, the interpolated CMC for all three initial CPC retentate concentration and equilibrium times are summarized in Table 2.1. The interpolated CMC values are all about 1mM which is consistent with the CMC measured from surface tension. This agreement is a necessary condition to establish the validity of the SED technique. The results show that the initial surfactant retentate concentration in the studied range (10 to 250 times the CMC) doesn't have a significant effect on the monomer concentration obtained from the SED experiment, consistent with only a slowly changing monomer concentration with total surfactant concentration above the CMC. Above the CMC, the slope of the interpolation line only slightly increases with increasing initial retentate CPC concentration, again supporting a very small dependence of monomer concentration on total surfactant concentration above the CMC. In Figs. 2.3 and 2.4, at about 8 and 4 times the equilibration time, there is a nearly discontinuous increase in permeate concentration which is reproducible, although not easy to explain. The change in the permeate solution volume due to osmotic effects leaving a portion of the membrane unwet could be an explanation. This effect does not affect the validity of the SED technique to obtain monomer-micelle equilibrium, although the data at times greater than when this jump occurs must be discarded in drawing interpolation curves.

From Fig. 2.2-2.4 and Table 2.1, the equilibration time is at 6.6, 5.3 and 2.25 hours for the initial surfactant retentate concentration of 10, 20 and 250 times the CMC of CPC, respectively. Micelle lifetimes are extremely short[94,95,99-101] (on the order of 10

msec) with exchange times for monomer entering/exiting micelles resulting in monomer residence time in micelles of microseconds scale[99-101]. So, the equilibration time dependence on retentate surfactant concentration is probably due to slow diffusion of surfactant across the unmixed retentate compartment to reach the membrane to diffuse across, not the rapid equilibration between monomer and micelles as monomer disappears into the membrane. It would seem that the straight line drawn through the data below the CMC should go through the origin (zero time, zero concentration), but it begins at a finite surfactant concentration at zero time, probably due to residual soak solution in the membrane leaching into the permeate solution at very short times.

Higher initial surfactant concentration in the retentate side promotes a higher osmotic pressure difference across the membrane. This osmotic effect causes the permeate solution volume to decrease after contact with the retentate solution. The difference in this volume increases as a function of time and initial retentate surfactant concentration. This volume difference has been found in the range of 1.5-60%.

2.3.3 Effect of Electrolyte Concentration for an Anionic Surfactant

From Table 2.1, we see that the anionic surfactant SDS has 6.5 times the CMC of cationic surfactant CPC. Fig. 2.5 shows permeate SDS concentration as a function of time for an initial retentate SDS concentration of 10 times the CMC. As with CPC, there are two clear linear regions in the kinetic curve in Fig. 2.5, although the difference in slope between the two regions is less than for CPC (Figs. 2.2-2.4) which can be attributed to the higher CMC of SDS.

The CMC from interpolation in Fig. 2.4 is 6.7×10^{-3} M, which agrees well with 6.5×10^{-3} M from surface tension measurements. The equilibration time is 8.0 hr, which

is longer than that for CPC when interpolating to the same initial retentate surfactant concentration as seen in Table 2.1. The slopes of both lines in Fig. 2.5 for SDS are much higher than these for CPC at any initial retentate concentration shown in Figs. 2.2-2.4. At low times, this is because there is a greater concentration driving force across the membrane due to the higher CMC. At times beyond when the CMC is attained, the higher slope indicates that the monomer activity increases with total surfactant concentration more rapidly than for CPC, again characteristic of a higher CMC ionic surfactant.

Figs. 2.6 and 2.7 show permeate surfactant concentration as a function of time for SDS with 0.1 M NaCl and 0.2 M NaCl, respectively. Initial retentate SDS concentrations are 10 times the CMC, which decreases with increasing [NaCl] as shown in Table 2.1. Two clear linear regions of the kinetic curve are observed. The CMC from interpolation at 0.1 M NaCl and 0.2 M NaCl are 1.25×10^{-3} M and 9.0×10^{-4} M, respectively. These values compared very favorably with the 1.15×10^{-3} M and 8.0×10^{-4} M CMC values obtained from surface tension measurements, respectively, as seen in Table 2.1. Thus, excellent agreement between the CMC values from SED and surface tension is again observed. The equilibration time does not change systematically with salinity (see Table 2.1 and Figs. 2.5, 2.6 and 2.7). The slope of both linear regions of the kinetic curves decreases with increasing salinity due to reduced CMC values. The lack of a systematic trend in equilibration time emphasizes that kinetic data must be obtained to calculate the CMC from SED data. Selecting a time to sample the permeate to measure retentate monomer concentrations does not appear to be feasible at this time.

The change in the permeate solution volume during a 4 day contact period is 30% for no added NaCl system, 10% for 0.1 M NaCl and 0% for 0.2 M NaCl. The initial permeate solution contains the same salinity as the retentate, so at a high enough [NaCl], the surfactant in the initial retentate solution adds insignificantly to the total dissolved species concentration, so osmotic pressure across the membrane becomes negligible. The anomalous jumps in permeate surfactant concentration at longer times seen for CPC were not observed for the three SDS experiments in Figs. 2.5-2.7.

2.3.4 Effect of Use of a Nonionic Surfactant

Fig. 2.8 shows the permeate surfactant concentration as a function of time for nonionic surfactant at an initial retentate $NP(EO)_{10}$ concentration of $3.6x10^{-4}$ M or 10 times the CMC with 0.2 M NaCl. The added NaCl has little effect on the micelle forming properties of nonionic surfactant (like CMC[95]), but is added here for convenience to avoid significant osmotic pressures. Three linear regions are observed. Two linear lines are drawn at low and medium times and the CMC from interpolation of the two lines is $3.7x10^{-5}$ M which agrees well with the CMC from surface tension at $3.6x10^{-5}$ M.

As seen in Table 2.1, the equilibration time is in the same range as that of the anionic and cationic surfactant systems. The three linear regions of the kinetic curve for $NP(EO)_{10}$ in Fig. 2.8 is probably a consequence of the polydispersity of the commercial nonionic surfactants. While a monodisperse nonionic surfactant would certainly have been preferable for this study, these were not readily available. Since nonionic surfactants generally have CMC values well below these of ionic surfactants[94,95,102], the permeate surfactant concentration requiring measurement in this

SED technique can be on the order of $1x10^{-5}$ M (see Fig. 2.8). In a mixture with a dissimilar surfactant when applied to monomer-micelle equilibrium determination in a mixed surfactant system generally requiring HPLC analysis and detectors applicable to surfactants without chromophores (e.g., evaporative light scattering), there is great difficulty measuring concentrations this low). Hence, for purposes of demonstrating the SED technique here, we choose a nonylphenol hydrophobe in the surfactant which can be detected by UV detectors to low concentrations. As analytical techniques continue to improve in the future, this should not be a fundamental limitation of the SED technique for nonionic surfactants.

2.4 CONCLUSIONS

In this study, the SED technique has been successfully established as a simple experimental method to measure the monomer-micelle equilibrium for single surfactant system, anionic, cationic or nonionic surfactant showing excellent agreement with CMC values from surface tension measurements. The results demonstrate that the initial retentate surfactant concentration and the added electrolyte concentration affect the kinetics of permeate surfactant concentration and osmotic pressure but not the interpolated monomer concentration. Although the interpolated monomer concentration is not affected by those parameters, minimizing the osmotic pressure makes experiments easier to perform. Therefore, for further study the initial condition will be at 10 times the CMC of studied surfactant system and 0.2 M NaCl. In Part II of this series, the binary surfactant mixture will be examined for the validity of this technique to measure mixed monomer-micelle equilibrium.

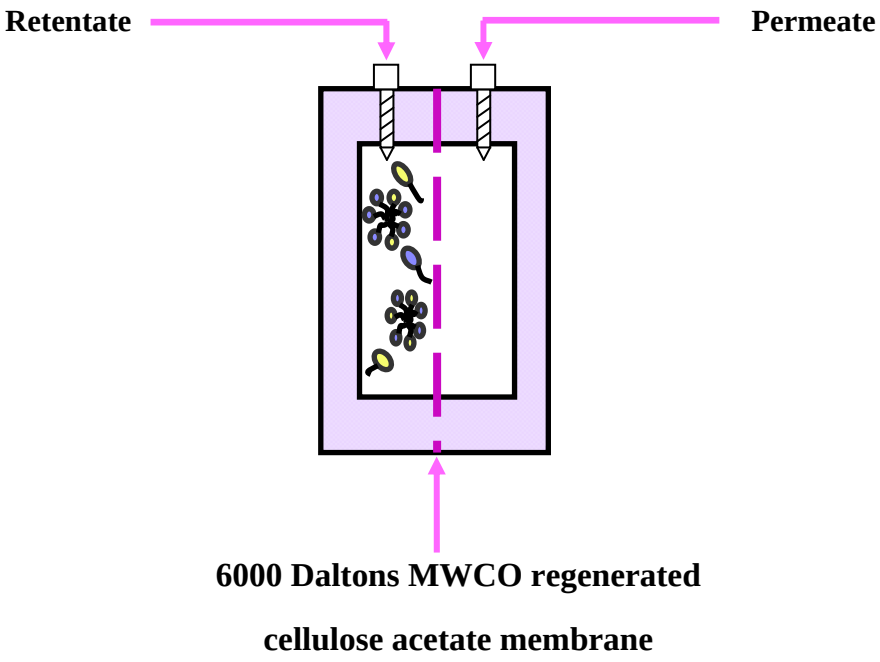

Figure 2.1 Illustration of semiequilibrium dialysis (SED) cell.

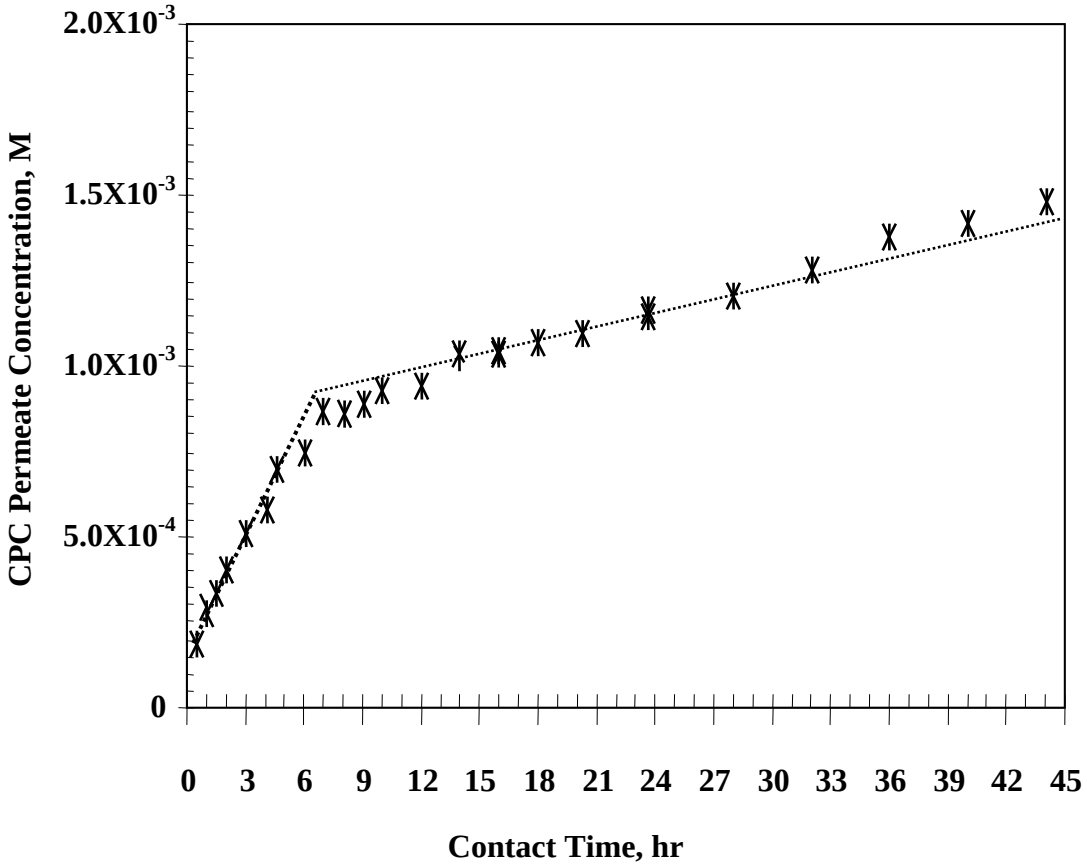

Figure 2.2 Kinetic results for permeate CPC concentration at $1x10^{-2}$ M initial CPC concentration.

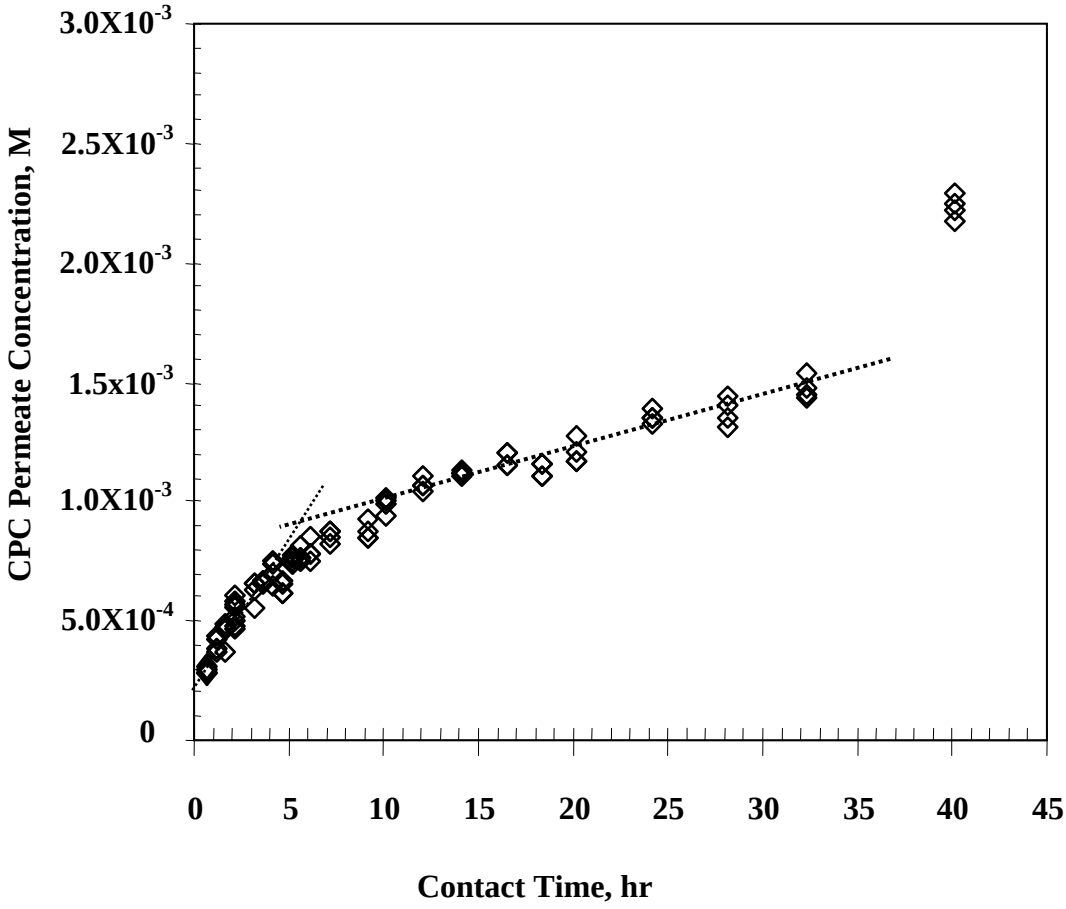

Figure 2.3 Kinetic results for permeate CPC concentration at $2x10^{-2}$ M initial CPC concentration in retentate.

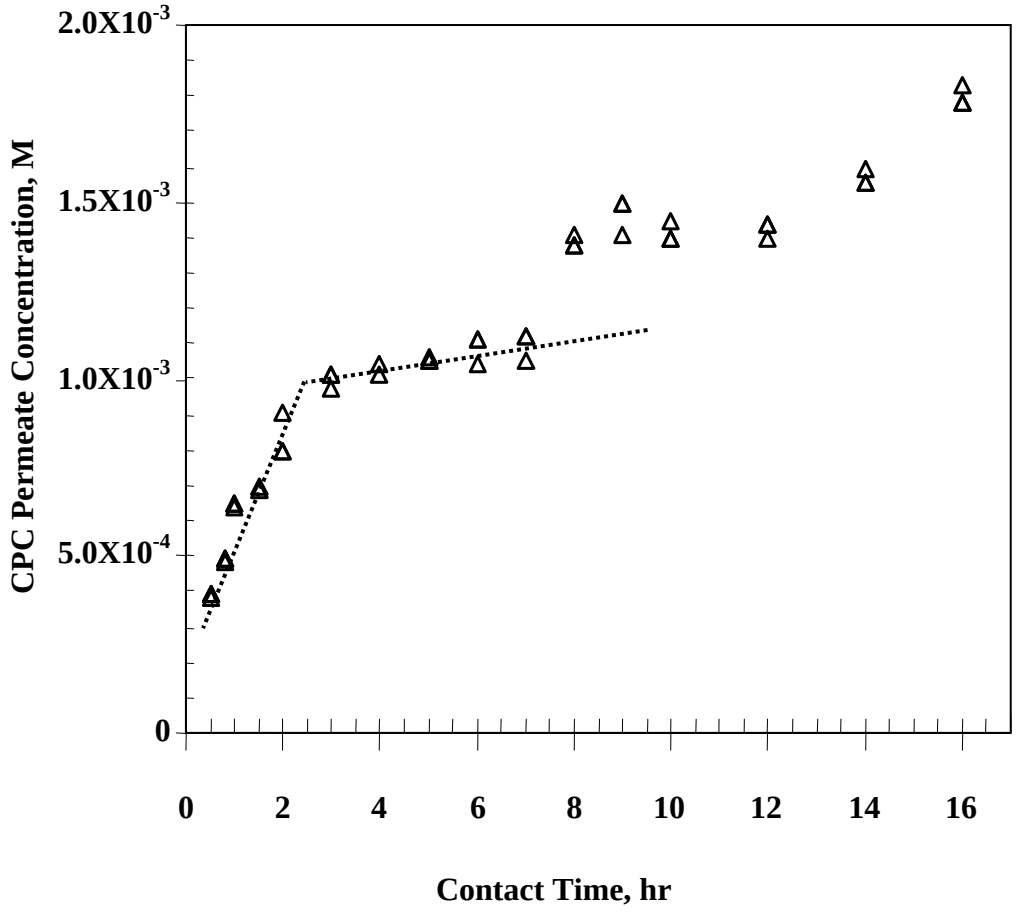

Figure 2.4 Kinetic results for permeate CPC concentration at $2.5x10^{-1}$ M initial CPC concentration in retentate.

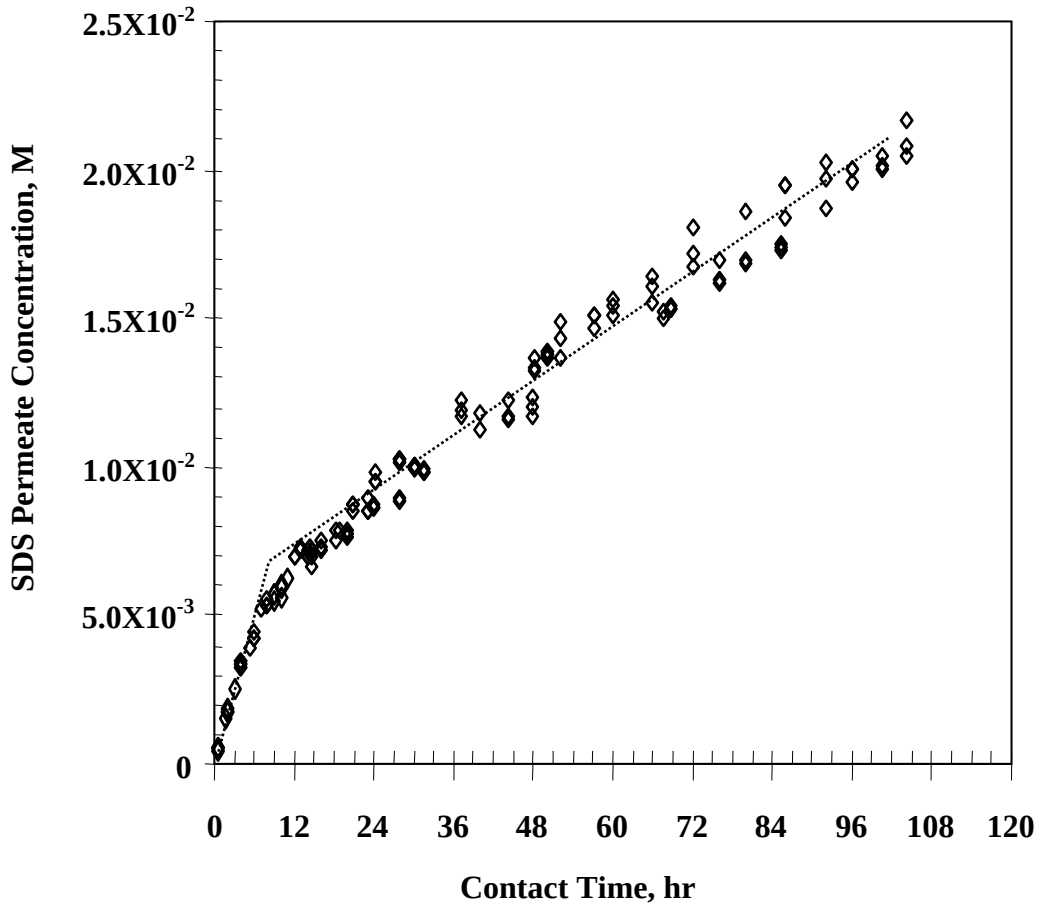

Figure 2.5 Kinetic results for permeate SDS concentration at $6.5x10^{-2}$ M initial SDS concentration in retentate.

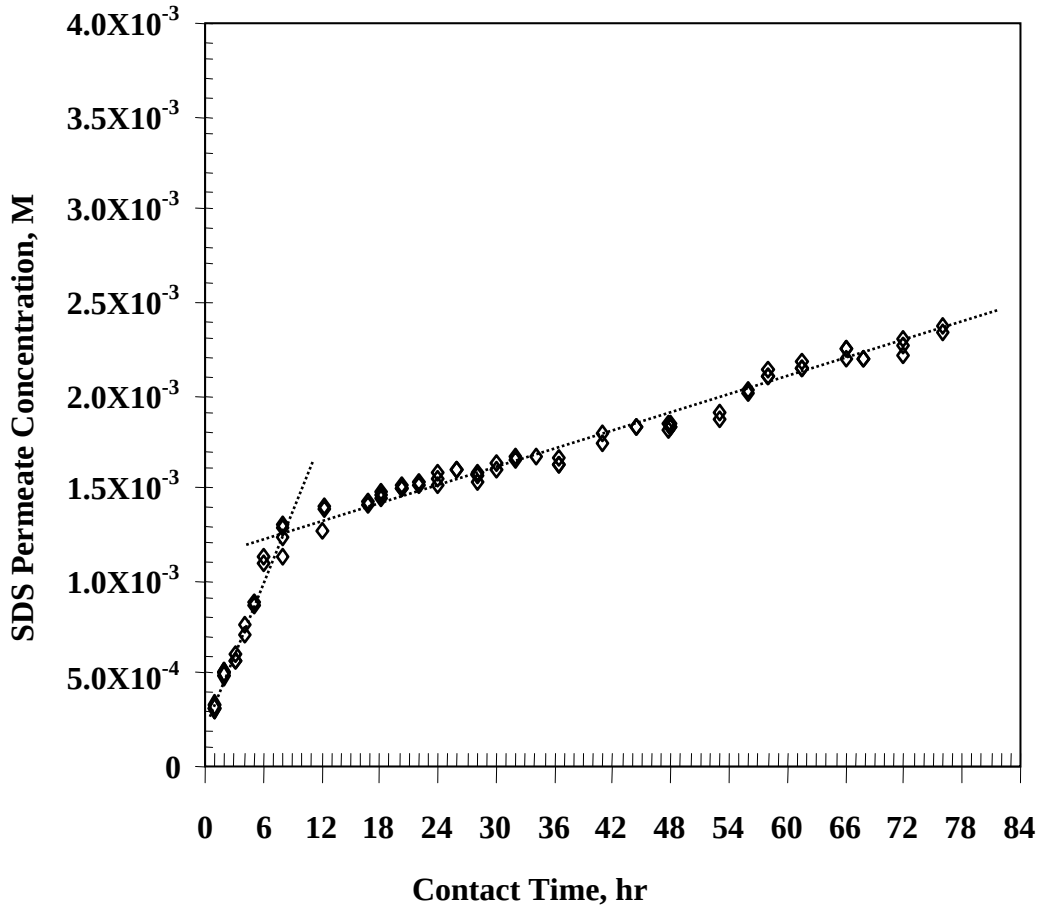

Figure 2.6 Kinetic results for permeate SDS concentration at 1.15×10^{-2} M initial SDS concentration in retentate and 0.1 M NaCl.

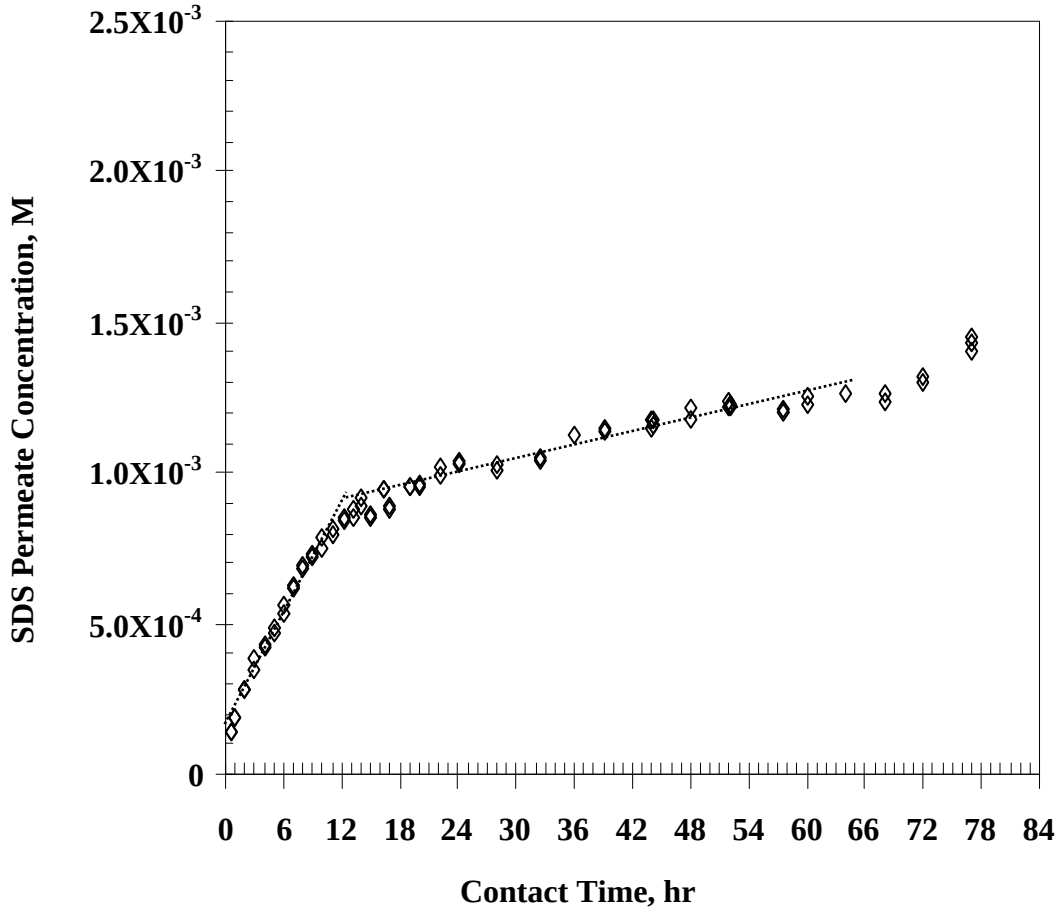

Figure 2.7 Kinetic results for permeate SDS concentration at 8.0×10^{-3} M initial SDS concentration in retentate and 0.2 M NaCl.

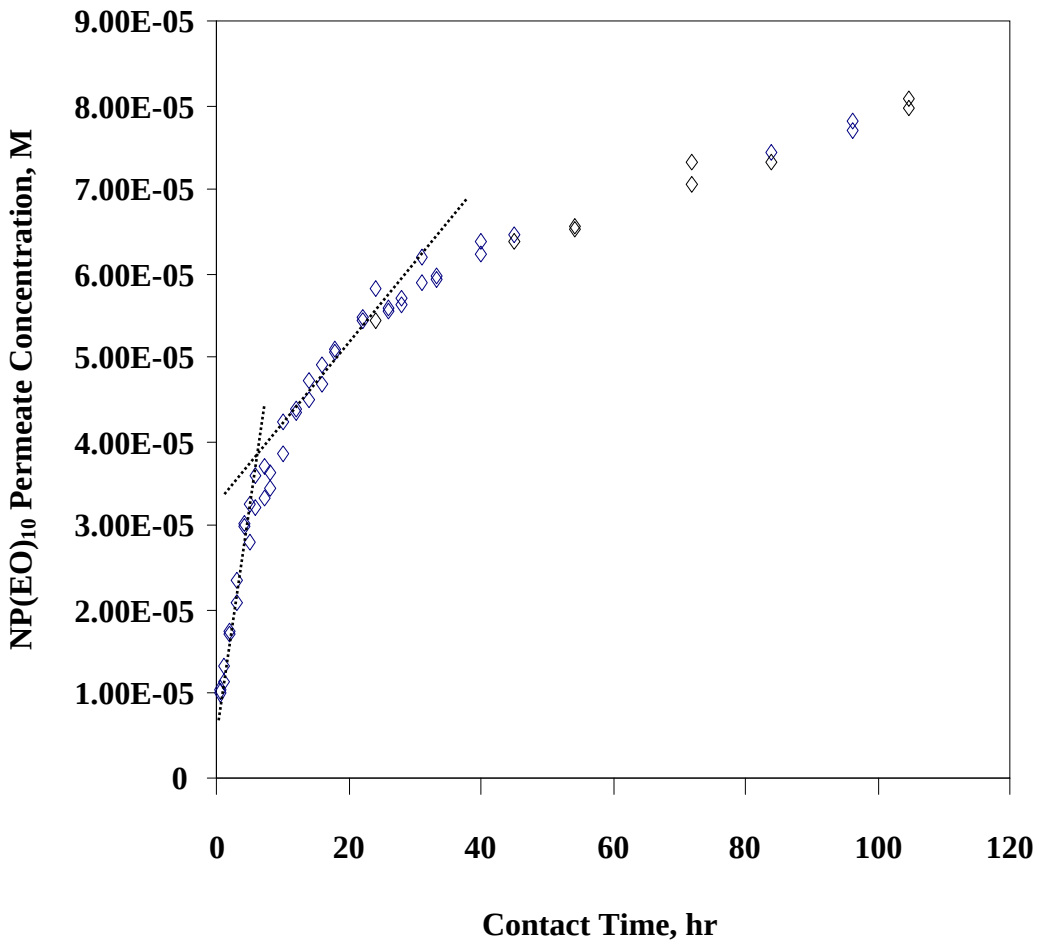

Figure 2.8 Kinetic results for permeate $NP(EO)_{10}$ concentration at $3.6x10^{-4}$ M initial $NP(EO)_{10}$ concentration in retentate and 0.2 M NaCl.

Table 2.1 CMC and equilibration time of single surfactants.

Surfactant	Initial Retentate Concentration (M)	NaCl Concen-tration (M)	CMC from Surface Tension (M)	CMC Interpolated from SED data (M)	Equilibration Time (Hr)
CPC	$1.0x10^{-2}$	0	$1.00x10^{-3}$	$8.8x10^{-4}$	6.6
CPC	$2.0x10^{-2}$	0	$1.00x10^{-3}$	$9.2x10^{-4}$	5.3
CPC	$2.5x10^{-1}$	0	$1.00x10^{-3}$	$1.0x10^{-3}$	2.25
SDS	$6.5x10^{-2}$	0	$6.50x10^{-3}$	$6.7x10^{-3}$	8.0
SDS	$1.15x10^{-2}$	0.1	$1.15x10^{-3}$	$1.25x10^{-3}$	8.0
SDS	$8.0x10^{-3}$	0.2	$8.00x10^{-4}$	$9.0x10^{-4}$	12.0
$NP(EO)_{10}$	$3.6x10^{-4}$	0.2	$3.6x10^{-5}$	$3.7x10^{-5}$	7.0

2.5 REFERENCES

1. Osborne-Lee, I.; Schechter, R. S.; Wade, W. H. *J. Colloid Interface Sci.* **1983**, 94, 179.

2. Warr, G.; Grieser, F.; Healey, T. W. *J. Phys. Chem.* **1983**, *87*, 1220.

3. Osborne-Lee, I.; Schechter, R. S.; Wade, W. H.; Barakat, Y. *J. Colloid Interface Sci.* **1985**, *108*, 60.

4. Grieser, F.; Healy, T. W.; Hsu, W.; Kratohvil, J.; Warr, G. *Colloids Surf.* **1989**, *42*, 97.

5. Asakawa, T.; Johten, K.; Miyagishi, S.; Nishida, N. *Langmuir* **1988**, *4*, 136.

6. Makayssi, A.; Lemordant, D.; Treiner, C. *Langmuir* **1993**, *9*, 2808.

7. Huang, L.; Somasundaran, P. *Langmuir* **1996**, *12*, 5790.

8. Hall, D. G.; Price, T. *J. Chem. Soc., Faraday Trans.* **1984**, *80*, 1193.

9. Rathman, J.; Scamehorn, J. F. *J. Phys. Chem.* **1984**, *88*, 5807.

10. Rathman, J.; Scamehorn, J. F. *Langmuir* **1989**, *3*, 372.

11. Treiner, C.; Khodja, A.; Fromon, M. *J. Colloid Interface Sci.* **1989**, *128*, 416.

12. Treiner, C.; Fromon, M.; Mannebach, M. *Langmuir* **1989**, *5*, 283.

13. Treiner, C.; Mannebach, M. *Colloid Polym. Sci.* **1990**, *268*, 88.

14. Bandyopadhyay, A.; Moulik, S. *Colloid Polym. Sci.* **1988**, *266*, 455.

15. Vikingstadt, E.; Kvammen, O. *J. Colloid Interface Sci.* **1980**, *74*, 16.

16. Zana, R.; Yiv, S.; Strazielle, C.; Lianos, P. *J. Colloid Interface Sci.* **1981**, *80*, 208.

17. Bostrom, G.; Backlund, S.; Blokhus, A.; Hoiland, H. *J. Colloid Interface Sci.* **1989**, *128*, 169.

18. Zana, R.; Djavanbakht, A. *Tenside, Surfactants, Deterg.* **1989**, *26*, 227.

19. Filipovic-Vincenkovic, N.; Skrtic, D. *Colloid Polym. Sci.* **1988**, *266*, 954.

20. Nakano, T. Y.; Sugihara, G.; Nakashima, T.; Yu, S. C. *Langmuir* **2002**, *18*, 8777.

21. Palous, J. L.; Turmine, M.; Letellier, P. *J. Phys. Chem. B* **1998**, *102*, 5886.

22. Peyre, V.; Letellier, P. *J. Colloid Interface Sci.* **1999**, *213*, 371.

23. Peyre, V. *Langmuir* **2002**, *18*, 1014.

24. Peyre, V.; Baillet, S.; Letellier, P. *Anal. Chem.* **2000**, *72*, 2377.

25. Gharibi, H.; Razavizadeh, B. M.; Hashemianzaheh, M. *Colloids Surf., A* **2000**, *174*, 375.

26. Sepulveda, L.; Cabrera, W. *J. Colloid Interface Sci.* **1989**, *131*, 8.

27. Abuin, E.; Lissi, E.; Nunez, R.; Olea, A. *Langmuir* **1989**, *5*, 753.

28. Koshinuma, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2341.

29. Yamishita, F.; Perron, G.; Desnoyers, J.; Kwak, J. *J. Colloid Interface Sci.* **1986**, *114*, 548.

30. Hierrezuelo, J. M.; Aguiar, J.; Ruiz, C. C. *Colloids Surf., A* **2005**, *264*, 29.

31. Corti, M.; Degiorgio, B.; Ghidoni, R.; Sonnino, S. *J. Phys. Chem.* **1983**, *86*, 2533.

32. Hoyer, H.; Doerr, I. *J. Phys. Chem.* **1964**, *68*, 3494.

33. Kaler, E.; Puig, J.; Miller, W. *J. Phys. Chem.***1984**, *88*, 2887.

34. Yu, Z.; Zhao, G. *J. Colloid Interface Sci.* **1989**, *130*, 414.

35. Yu, Z.; Zhao, G. *J. Colloid Interface Sci.* **1989**, *130*, 421.

36. Al-Saden, A.; Florence, A.; Whateley, T., Puiseux, F.; Vaution, C. *J. Colloid Interface Sci.* **1982**, *86*, 51.

37. Yedgar, S.; Barenholz, Y.; Cooper, V. *Biochim. Biophys. Acta* **1974**, *363*, 98.

38. Dennis, E. *Arch. Biochem. Biophys.* **1974**, *165*, 764.

39. Corti, M.; Degiogio, V.; Sonnino, S.; Ghidoni, R.; Masserini, M.; Tettamanti, G. *Chem. Phys. Lipids* **1981**, *28*, 197.

40. Cantu, L.; Corti, M.; Degiorgio, V. *J. Phys. Chem.* **1990**, *94*, 793.

41. Svard, M.; Schurtenberger, P.; Fontell, K.; Jonsson, B.; Lindman, B. *J. Phys. Chem.* **1988**, *92*, 2261.

42. Schurtenberger, P.; Bertani, R.; Kanzig, W. *J. Colloid Interface Sci.* **1986**, *114*, 82.

43. Edwards, K.; Almgren, M.; Bellare, J.; Brown, W. *Langmuir* **1989**, *5*, 473.

44. Dubin, P.; The, S.; McQuigg, D.; Chew, C.; Gan, L. *Langmuir* **1989**, *5*, 89.

45. Dubin, P.; Chew, C.; Gan, L. *J. Colloid Interface Sci.* **1989**, *128*, 566.

46. Ionescu, L.; Picot, C.; Duval, M.; Duplessix, R.; Benoit, H. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1019.

47. Zana, R.; Picot, C.; Duplessix, R. *J. Colloid Interface Sci.* **1983**, *93*, 43.

48. Burkitt, S.; Ottewill, R.; Hayter, J.; Ingram, B. *Colloid Polym. Sci.* **1987**, *265*, 628.

49. Hendrikx, Y.; Charvolin, J.; Rawiso, M. *J. Colloid Interface Sci.* **1984**, *100*, 597.

50. Alperine, S.; Hendricks, Y.; Charvolin, J. *J. Phy. Lett. (Paris)* **1985**, *46*, 27.

51. Lin, T.; Chen, S.H.; Gabriel, N.; Roberts, M. *J. Phys. Chem.* **1990**, *94*, 855.

52. Griffiths, P. C.; Whatton, M. L.; Abbott, R. J.; Kwan, W.; Pitt, A. R.; Howe, A. M.; King, S. M.; Heenan, R. K. *J. Colloid Interface Sci.* **1999**, *215*, 114.

53. Griffiths, P. C.; Paul, A.; Khayat, Z.; Heenan, R. K.; Ranganathan, R.; Grillo, I. *Soft Matter* **2005**, *1*, 152.

54. Penfold, J.; Staples, E.; Tucker, I.; Thomas, R. K. *Langmuir* **2004**, *20*, 1269.

55. Penfold, J.; Staples, E.; Thompson, L.; Tucker, I.; Hines, J.; Thomas, R. K.; Lu, J. R.; Warren, N. *J. Phys. Chem. B* **1999**, *103*, 5204.

56. Tokina, F.; Tsujii, K. *J. Colloid Interface Sci* **1972**, *41*, 343.

57. Bansal, V.; Biswas, A.; Balusubramanian, D. *Colloid Polym. Sci.* **1979**, *257*, 1083.

58. Asakawa, T.; Miyagishi, S.; Nishida, M. *J. Colloid Interface Sci.* **1985**, *104*, 279.

59. de Weerd, R.; de Hann, J.; van de Ven, L.; Achten, M.; Buck, H. *J. Phys. Chem.* **1982**, *86*, 2523.

60. de Weerd, R.; de Haan, J.; van de Ven, L.; Buck, H. *J. Phys. Chem.* **1982**, *86*, 2528.

61. Barker, C.; Saul, D.; Tiddy, G.; Wheeler, B.; Willis, E. *J. Chem. Soc., Faraday Trans.* **1974**, *70*, 154.

62. Nilsson, P. G.; Lindman, B. *J. Phys. Chem.* **1984**, *88*, 5391.

63. Kato, T.; Iwai, M.; Seimiya, T. *J. Colloid Interface Sci.* **1989**, *130*, 439.

64. Jansson, M.; Linse, P.; Rymden, R. *J. Phys. Chem.* **1988**, *92*, 6689.

65. Guering, P.; Nilsson, P. G.; Lindman, B. *J. Colloid Interface Sci.* **1985**, *105*, 41.

66. Jansson, M.; Rymden, R. *J. Colloid Interface Sci.* **1987**, *119*, 185.

67. Jansson, M.; Jonsson, B. *J. Phys. Chem.* **1989**, *93*, 145.

68. Calfors, J.; Stilbs, P. *J. Phys. Chem.* **1984**, *88*, 4410.

69. Stilbs, P. *J. Colloid Interface Sci.* **1982**, *89*, 547.

70. Calfors, J.; Stilbs, P. *J. Colloid Interface Sci.* **1985**, *103*, 332.

71. Faucompre, B.; Lindman, B. *J. Phys. Chem.* **1987**, *91*, 383.

72. Soderman, O.; Stilbs. P. *Prog. Nucl. Magn. Reson. Spectrosc.* **1994**, *26*, 445.

73. Stilbs, P. *Prog. Nucl. Magn. Reson. Spectrosc.* **1987**, *19*, 1.

74. Eads, C. D.; Robosky, L. C. *Langmuir* **1999**, *15*, 2661.

75. Ciccarelli, D.; Costantino, L.; D'Errico, G.; Paduano, L.; Vitagliano, V. *Langmuir* **1998**, *14*, 7130.

76. Staples, E.; Thomspon, L.; Tucker, I.; Penfold, J.; Thmoas, R.K.; Lu, J.R. *Langmuir* **1993**, *9*, 1651.

77. Penfold, J.; Staples, E.; Tucker, I.; Creeth, A.; Hines, J.; Thompson, L.; Cummins, P.; Thomas, R.K.; Warren, N. *Colloids Surf., A* **1997**, *128*, 107.

78. Penfold, J.; Staples, E.; Tucker, I.; Thomas, R.K. *Langmuir* **2004**, *20*, 1269.

79. Penfold, J.; Thomas, R.K.; Dong, C.C.; Tucker, I.; Metcalfe, K.; Golding, S.; Grillo, I. *Langmuir* **2007**, *23*, 10140.

80. Lee, H.; Deo, N.; Samasundaran, P. *J. Disp. Sci. Technol.* **2002**, *23*, 483.

81. Zhang, R.; Somasundaran, P. *Langmuir* **2004**, *20*, 8552.

82. Deo, P.; Deo, N.; Somasundaran, P. *Langmuir* **2005**, *21*, 9998.

83. Imamura, H.; Tsuchiya, K.; Kondo, Y.; Yoshino, N.; Ohkubo, T.; Sakai, H.; Abe, M. *J. Oleo Sci.* **2005**, *54*, 125.

84. Christian, S. D.; Smith, G. A.; Tucker, E. E.; Scamehorn, J. F. *Langmuir* **1985**, *1*, 564.

85. Mahmoud, F. Z.; Christian, S. D.; Tucker, E. E.; Taha, A. A.; Scamehorn, J. F. *J. Phy. Chem.* **1989**, *93*, 5903.

86. Lee, B. H.; Christian, S. D.; Tucker, E. E.; Scamehorn, J. F. *Langmuir* **1991**, *7*, 1332.

87. Christian, S. D.; Tucker, E. E.; Scamehorn, J. F.; Uchiyama, H. *Colloid Polym. Sci.* **1994**, *272*, 745.

88. Rouse, J. D.; Sabatini, D. A.; Deeds, N. R.; Brown, R. E.; Harwell, J. H. *Environ. Sci. Technol.* **1995**, *29*, 2484.

89. Saito, Y.; Miura, K.; Tokuoka, Y.; Kondo, Y.; Abe, M.; Sato, T. *J. Disp. Sci. Technol.* **1996**, *17*, 567.

90. Gelinas, S.; Weber, M. E. *Sep. Sci. Technol.* **1998**, *33*, 1241.

91. Rouse, J. D.; Bjornen, K. K.; Taylor, R. W.; Shiau, B.-J., *Environ. Pract.* **2004**, *6*, 157.

92. Nguyen, C. M.; Christian, S. D.; Scamehorn, J. F. *Tenside, Surfactants, Deterg.* **1988**, *25*, 328.

93. Rodriguez, C. H.; Lowery, L. H.; Scamehorn, J. F.; Harwell, J. H. *J. Surfactants Deterg.* **2001**, *4*, 1.

94. Scamehorn, J. F.; Sabatini, D. A.; Harwell, J. H. In *Encyclopedia of Supramolecular Chemistry*; Atwood, J., Stead, J., Eds; Marcel Dekker: New York, 2004; p 1458-1469.

95. Rosen, M. J. *Surfactants and Interfacial Phenomena*, 3rd ed.; Wiley: New York, 2004; Chapter 3.

96. Corrin, M.L.; Harkins, W. D. *J. Am. Chem. Soc.* **1947**, *69*, 683.

97. Williams, R.J.; Philips, J.N.; Mysels, K.J. *Trans Faraday Soc.* **1955**, *51*, 728.

98. Schulz, P.C. *Colloids Surf.* **1988**, *34*, 69.

99. Patist, A.; Jha, B.K.; Oh, S.G.; Shah, D.O. *J. Surfactants Deterg.* **1999**, *2*, 317.

100. Dhara, D.; Shah, D.O. *J. Phys. Chem.* **2001**, *105*, 7133.

101. Wong, T. C. In *Encyclopedia of Surface and Colloid Science Volume 5*; Somasundaran, P., Eds.; CRC Press: Florida, 2006; 3738-3756.

102. Rosen, M. J. In *Mixed Surfactant Systems*; Holland, P. M., Rubingh, D. N., Eds.; ACS Symposium Series No. 501; American Chemical Society: Washington DC, 1991; p 316-326.

CHAPTER 3

Measuring Monomer-Micelle Equilibrium by Using Semi-Equilibrium Dialysis. II. Anionic/Nonionic and Cationic/Nonionic Surfactant Systems

In the Part I of this series of three papers, the semi-equilibrium dialysis (SED) technique for measuring monomer-micelle equilibrium was validated for single surfactants. Here in part II, the monomer-micelle equilibrium of binary mixtures of ionic and nonionic surfactants has been measured by this experimental method. By using a linear interpolation technique developed in Part I, the individual monomer concentrations can be obtained from a plot of permeate surfactant concentration vs. time. The mixed CMC values obtained from this SED technique agree well with those from surface tension measurements. The experimental results are also compared to the predicted values from often-used regular solution theory (RST). The critical micelle concentration (CMC) of the studied mixtures are well correlated to RST results with an interaction parameter typical of ionic/nonionic surfactant mixtures. However, the predictions of the micellar composition at a given monomer composition from RST deviate from the experimental results. In one case, even the wrong surfactant component is predicted to be enriched in micelles compared to monomer.

3.1 INTRODUCTION

In many surfactant applications (e.g. laundry detergents), surfactant mixtures are commonly used because of mixture synergisms in performance and because most commercial surfactants (e.g., linear alkylbenzene sulfonates and ethoxylated alcohols) are naturally mixtures. Monomer-micelle equilibrium, the distribution of surfactant species between the monomer and the micelles in solution, dictates many important physical properties of surfactants[1-4]. For multicomponent surfactant systems, one important feature is the difference in the micellar composition as compared to the monomer and overall compositions. Although monomer-micelle equilibrium compositions have been experimentally determined by using different methods[5-15], these experimental measurements have limitations (e.g., expensive, difficult to interpret the data, and only applicable to specific systems). The goal of this work is to develop a universal, inexpensive, user-friendly technique to measure monomer-micelle equilibrium.

Various mathematical models to describe monomer-micelle equilibrium have been proposed. These models include the mass action model[16-18], the pseudophase separation model[2,13,19-23], the group contribution method[24-28], the Gibbs-Duhem equation[21,24-35], regular solution theory (RST) [12,13,36-46], a model based on conductivity measurement[47], and molecular thermodynamic models[48-57].

By far the most commonly used thermodynamic model used to describe practical surfactant systems is RST, also referred to as nonideal solution theory[58], or generically as a one-parameter Margules equation[59]. This model is so popular because it is a one-parameter model which accurately describes CMC data for surfactant mixtures. However, the CMC is related to the Gibbs free energy which is a relatively

insensitive parameter: a number of models can fit CMC data as a function of monomer composition relatively well. Nonetheless, this does not mean that the composition of micelles in equilibrium with a given monomer composition is accurately predicted by RST as the CMC is the minimum total monomer concentration at which micelles form with no information about the composition of these micelles. This paper compares measured micelle compositions to those predicted from RST for nonideal ionic/nonionic surfactant mixtures. When a surfactant composition is varied, the excess free energy of mixing on mixed micelle formation can be unsymmetrical[60], in contrast to the symmetry which is prediction by RST. In Part III of this series[61], the excess enthalpy and excess entropy of mixed micelle formation, determined by the temperature dependence of monomer-micelle equilibrium measured using the SED technique, will be compared to predictions from RST.

Typically, the RST interaction parameter (β) is calculated for a given monomer composition from the measured CMC of the mixture. While here we will only consider binary surfactant systems, generalization to more components is straightforward[36]. To use RST for binary surfactant systems, if the CMC of the pure components (C_1^0 and C_2^0) and the mixed CMC (C_{12}) are measured as a function of monomer mole fraction of surfactant 1 (y_1), the interaction parameter (β) of these two surfactants and the mole fraction of surfactant 1 in the mixed micelle (x_1) can be calculated from the following equations obtained by equating the partial fugacity of each surfactant component in monomer and micelles:

$$y_1 C_{12} = x_1 C_1^0 e^{(\beta(1-x_1)^2)} \quad (1)$$

$$(1-y_1)C_{12} = (1-x_1)C_2^0 e^{(\beta x_1^2)} \quad (2)$$

The CMC is commonly obtained at several monomer compositions (y_1) and some best fit averaging procedure used to calculate a single β value for the surfactant system from the values at the individual compositions. Theoretical models have also been used to predict the β parameter for surfactant mixtures[62-66]. The RST assumes a constant interaction parameter (β) for particular surfactant mixture while many experiments observe a change in this parameter as a function of temperature and composition[Error! Bookmark not defined.,67-71]. After obtaining the β parameter, the mixed CMC (C_{12}) and the micelle composition (x_1) of this surfactant mixture can be predicted at any y_1 from simultaneous solution of equations 1 and 2.

3.2 EXPERIMENTAL SECTION

3.2.1 Materials

The same materials and purification procedures as Part I[72] were used in this work. The three surfactants studied were sodium dodecyl sulfate (SDS), cetylpyridinium chloride (CPC), and nonylphenol polyethoxylate with an average degree of polymerization of 10 ($NP(EO)_{10}$) and the salt used in this study was sodium chloride (NaCl).

3.2.2 Methods

Experimental methods for both CMC measurements and SED experiments were described in Part I[72]. The two studied surfactant mixtures were SDS/$NP(EO)_{10}$ and CPC/$NP(EO)_{10}$. The experimental conditions for all studies were 30°C and 0.2 M NaCl.

3.3 RESULTS AND DISCUSSION

3.3.1 CMC Determination and β Parameter Calculation

Surface tensions were measured and plotted as a function of total surfactant concentration. The CMC of the surfactant mixture is determined as the point where a sharp transition to a minimum surface tension is observed[73]. The CMC values measured here ($8.0x10^{-4}$ M for SDS, $4.0x10^{-5}$ M for CPC, $3.6x10^{-5}$ for $NP(EO)_{10}$) are consistent with literature values for the individual surfactants[74] at 30°C and 0.2 M NaCl.

The β parameter at each surfactant mixture ratio was calculated from experimental mixed CMC values by using equations (1) and (2). The average β values of SDS/$NP(EO)_{10}$ and CPC/$NP(EP)_{10}$ mixtures are -2.06 and -1.45, respectively. These β values are typical for ionic/nonionic surfactant systems[58] at this salinity.

3.3.2 Results from SED Experiments for Mixtures of Anionic and Nonionic Surfactants

The SED experiments were conducted at 30^{o}C to determine the permeate surfactant concentration at different contact times for SDS and NP(EO)$_{10}$ mixtures. Three different ratios (75/25, 50/50 and 25/75) of SDS/NP(EO)$_{10}$ mixtures were studied. The initial retentate concentration was at ten times the mixed CMC for each composition as shown in Table 3.1. To both retentate and permeate compartments, 0.2 M sodium chloride (NaCl) was added to prevent significant osmotic pressure gradients between retentate and permeate compartments and because swamping electrolyte simplifies the thermodynamic analysis when ionic surfactants are involved. Nonetheless, it should be noted that osmotic pressure gradients across the dialysis membrane do not invalidate the SED technique. The volume change would need to be taken into account in material balances if water passes through the membrane. Another solution is to seal the chambers to not permit bulk flow through the membrane. However, the membrane can bow under pressure gradients and even rupture if osmotic pressures are great enough. Our experience is that even at ionic strength differences of as much as 0.2 M between permeate and retentate compartments, the membrane retains its integrity. So, it was for experimental convenience in this work that the swamping electrolyte was used to demonstrate the validity of the measurement.

Figs. 3.1 – 3.3 show the permeate SDS and NP(EO)$_{10}$ concentrations as a function of time at different initial SDS/NP(EO)$_{10}$ ratios. These kinetic results show that the permeate surfactant concentration dramatically increases at early time followed by a reduction in the rate of increase in the permeate surfactant concentration with increasing time. Because the results of these mixtures are similar to those of single surfactant systems studied in Part I[72], the linear interpolation procedures developed

there are utilized to estimate the monomer concentration of each surfactant, as shown in Figs. 3.1-3.3 and summarized in Table 3.1.

To help in interpretation of the results, we will consider one initial composition in detail. For the case of 75/25 SDS/NP(EO)$_{10}$ initial mole fraction from Fig. 3.1, the interpolated monomer concentration of SDS and NP(EO)$_{10}$ are 2.25×10^{-4} M and 1.25×10^{-5} M, respectively. These monomer concentrations yield the mixed CMC of 2.38×10^{-4} M with SDS mole fraction in monomer (y_{SDS}) of 0.95 and NP(EO)$_{10}$ mole fraction in monomer ($y_{NP(EO)10}$) of 0.05. Knowing the mixed CMC, each monomer surfactant concentration, the total surfactant concentration and total surfactant ratio, the micelle composition in the retentate can be calculated. The SDS and NP(EO)$_{10}$ concentrations in micelles are thus calculated to be 3.00×10^{-4} M and 2.25×10^{-4} M, corresponding to SDS and NP(EO)$_{10}$ micellar mole fractions of 0.57 and 0.43, respectively. In applying a mass balance to calculate micellar concentrations of each surfactant in the retentate from initial concentrations and measured monomer concentrations, the surfactant lost to the permeate compartment must be included in the calculation. For instance, at the equilibration time, both SED compartments have surfactant monomer but only the retentate compartment contains surfactant micelles. In this work, both compartments contain the same solution volume throughout the experiment and there is minimal osmotic pressure due to identical swamping electrolyte in each compartment.

The mixed CMC, monomer and micellar compositions of studied SDS/NP(EO)$_{10}$ mixtures obtained from SED experiments presented in Figs. 3.1-3.3 are summarized in Table 3.1. The micelles are enriched in NP(EO)$_{10}$ compared to the

monomer for all three initial compositions studied. In all cases, this makes sense as the nonionic surfactant has a lower CMC and partitions more strongly into micelles.

Equilibration time is defined as the time at which equilibrium monomer concentration is reached in the permeate for a given surfactant component and is summarized in Table 3.1. As expected, the equilibration time is not generally the same for the dissimilar surfactants due to different diffusivities. This emphasizes the need to obtain the time dependency of permeate concentrations for each surfactant. There is no particular time at which samples would yield equilibrium compositions for both components. This is in contrast to the study of SED for measurement of solubilization equilibrium constants in micelles where there is a window of opportunity of about 18 to 24 hours[75] at which permeate samples contain the equilibrium solute concentration. Five of the six surfactants in Table 3.1 have an equilibration time of 8 to 12 hours. The exception is the case of $NP(EO)_{10}$ in the 75/25 SDS/$NP(EO)_{10}$ initial mole fraction system in which the equilibration time is 2 hours. This could be due to a relatively low $NP(EO)_{10}$ monomer concentration and a significant difference (20 times) between the initial $NP(EO)_{10}$ concentration and the $NP(EO)_{10}$ monomer concentration in this mixture. In contrast to $NP(EO)_{10}$, the SDS initial concentration in this mixture is only three times higher than the SDS monomer concentration. This results in the gradual change in the slope of the kinetic curve of SDS in this mixture, unlike a sharp change in the slope in the other curves. Further we note that the equilibration time of the mixture components is longer than the corresponding pure components from Part I[72] (times from 5 to 12 hours).

3.3.3 Results from SED Experiments for Mixtures of Cationic and Nonionic Surfactants

The CPC and $NP(EO)_{10}$ permeate concentrations are plotted as a function of contact time at 30°C with 0.2 M NaCl in Figs. 3.4-3.6 for three different ratios (75/25, 50/50 and 25/75) of CPC/$NP(EO)_{10}$. The initial retentate concentration was at ten times the mixed CMC for each composition as shown in Table 3.2. These kinetic data for CPC/$NP(EO)_{10}$ mixtures exhibit more scatter than those for SDS/$NP(EO)_{10}$. This may be due to the more similar CMC values for CPC and $NP(EO)_{10}$ (4.0×10^{-5} M and 3.6×10^{-5} M), yielding a similar thermodynamic activity gradient for both components across the membrane. Nonetheless, the CPC/$NP(EO)_{10}$ kinetic data still show a change in slope of permeate surfactant concentration vs. time which is suitable for using the linear interpolation technique to obtain the monomer concentration of each surfactant. The interpolated monomer concentrations for all three initial CPC/$NP(EO)_{10}$ ratios from Figs. 3.4 through 3.6, the mixed CMC, and calculated surfactant mole fraction in monomer and micelle are summarized in Table 3.2. The micelles are enriched in CPC relative to the monomer for all three initial compositions, although the enrichment is less significant in the SDS/$NP(EO)_{10}$ case, likely due to the more similar CMC values in the CPC/$NP(EO)_{10}$ case.

Because the mixed CMC of the studied CPC/$NP(EO)_{10}$ system is lower than the studied SDS/$NP(EO)_{10}$ system, the driving force (monomer activity) for the monomer species to diffuse from retentate to permeate is also less, which likely explains the longer equilibration time for the CPC/$NP(EO)_{10}$ system (between 15 and 54 hours) when compared to the SDS/$NP(EO)_{10}$ mixture (approximately 10 hours) (Tables 3.2

and 3.1, respectively). The equilibration time for the two surfactants in a given system can be quite different as seen in Table 3.2 (e.g., 15 hr vs. 54 hr).

The kinetic results from both SDS/NP(EP)$_{10}$ and CPC/NP(EO)$_{10}$ mixtures show that the equilibration time for the surfactant concentration in the permeate compartment to reach the surfactant monomer concentration varies significantly depending on the studied conditions (including initial concentration, initial surfactant ratio and the type of surfactant). These results demonstrate that it is crucial to obtain the kinetic data of each surfactant from the SED experiment in order to accurately determine the monomer and micelle composition.

3.3.4 Comparing the Results from SED Technique to the Predictions from RST

At a given monomer composition, the mixed CMC and micellar composition were obtained from the β parameter from surface tension derived CMC values and RST (equations 1 and 2). Figs 3.7 and 3.8 plot CMC as a function of ionic surfactant monomer mole fraction for SDS/NP(EO)$_{10}$ and CPC/NP(EO)$_{10}$ mixtures, respectively. In these plots, the reported CMC values came from three different sources: surface tension measurement, SED experiment and RST prediction based on the average β parameter from surface tension measurements. For both studied mixtures, the CMC values obtained from surface tension measurement and the SED technique agree with each other and are well correlated by the prediction from RST. Agreement between the total monomer concentration from the SED method and the measured CMC is a necessary condition for validity of SED measurements. The excellent agreement observed in Figs. 3.7 and 3.8 provides substantial support for the SED method proposed here.

The micellar mole fraction of SDS (x_{SDS}) in SDS/NP(EO)$_{10}$ mixture is plotted as a function of SDS monomer mole fraction (y_{SDS}) in Fig. 3.9. The dashed line represents the predicted values from RST. The RST predicts that x_{SDS} is always less than y_{SDS} for this mixture (no azeotrope) even though β is negative due to the wide difference in the CMC values of SDS and NP(EO)$_{10}$. The SDS micellar mole fraction obtained from the SED technique is higher than the values predicted by RST. The difference between the micellar mole fraction of SDS obtained from the experiment and RST is in the range of 19-44%.

Fig. 3.10 shows the relationship between CPC micellar and monomer mole fraction in the CPC/NP(EO)$_{10}$ mixture. An azeotrope ($y_{CPC} = x_{CPC}$) is at $y_{CPC} = 0.46$, below which the micelle is enriched in CPC compared to the monomer and above which the monomer is enriched in CPC compared to the micelles. From the data obtained from the SED technique, the micellar mole fraction of CPC is significant higher than the RST predictions. The difference between the experimental results and model prediction is in the range of 46 - 63%. Furthermore in one case, the SED technique measures an CPC-rich micelle ($y_{CPC} = 0.6$ and $x_{CPC} = 0.79$, Fig. 3.10) while the RST predicts a NP(EO)$_{10}$-rich micelle. The important conclusion is that RST predictions of monomer-micelle equilibrium can be in gross error with measured results even though RST predicts CMC values well.

3.4 CONCLUSIONS

In this Part II of the three part series, the SED technique has been used to measure the monomer micelle equilibrium of two ionic/nonionic surfactant binary mixtures at 30^{o}C.

The results demonstrate that the kinetic data are necessary to precisely determine the surfactant monomer and micelle compositions from the SED technique. In addition, the values of CMC obtained from this technique show excellent correlation with the data from surface tension measurement and predictions from RST. Finally, although RST describes the CMC data well, the predictions of monomer and micelle compositions from RST can be in gross error. Overall, these results further support the SED technique proposed here for assessing properties of multi-surfactant systems.

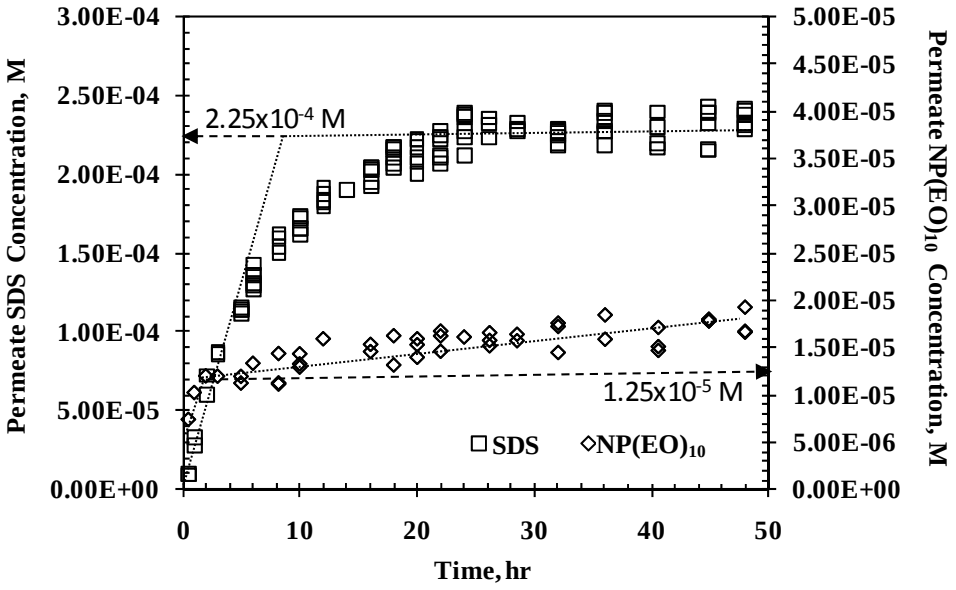

Figure 3.1 Kinetic results for permeate surfactant concentration from SED experiment at 75/25 initial SDS/$NP(EO)_{10}$ mole fraction, 0.2 M NaCl and 30^{o}C. Initial total surfactant concentration in retentate is $1x10^{-3}$ M (ten times the mixed CMC of this system).

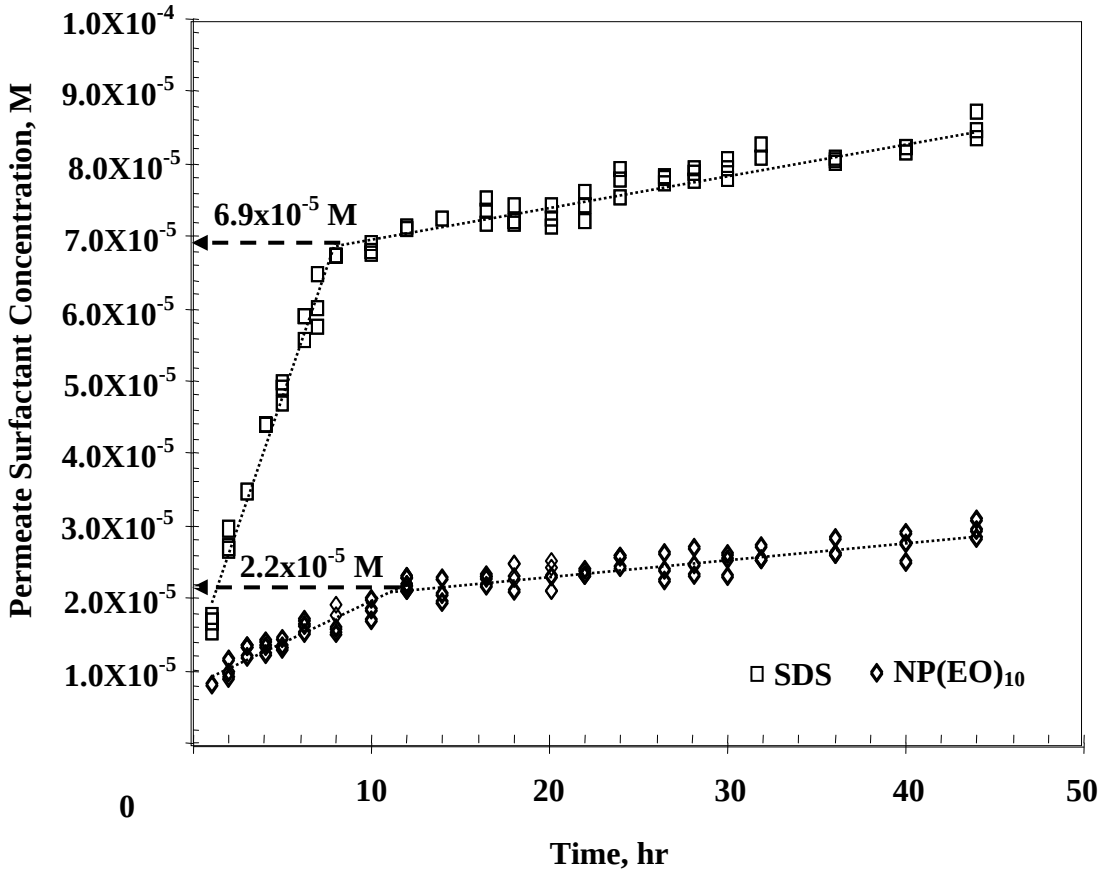

Figure 3.2 Kinetic results for permeate surfactant concentration from SED experiment at 50/50 initial SDS/$NP(EO)_{10}$ mole fraction, 0.2 M NaCl and 30^{o}C. Initial total surfactant concentration in retentate is $6x10^{-4}$ M (ten times the mixed CMC of this system).

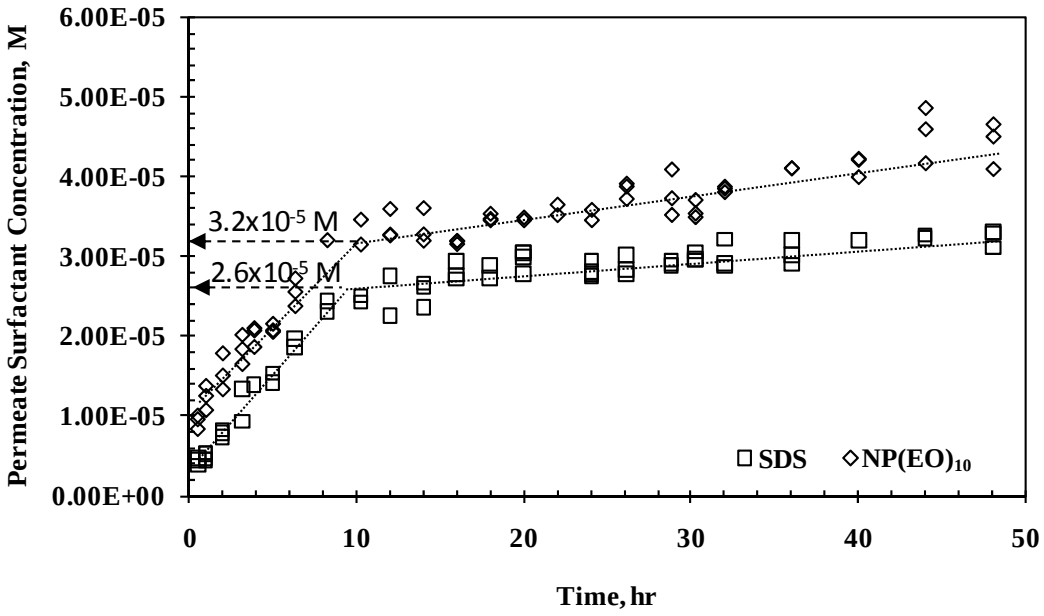

Figure 3.3 Kinetic results for permeate surfactant concentration from SED experiment at 25/75 initial SDS/$NP(EO)_{10}$ mole fraction, 0.2 M NaCl and 30^{o}C. Initial total surfactant concentration in retentate is $5.6x10^{-4}$ M (ten times the mixed CMC of this system).

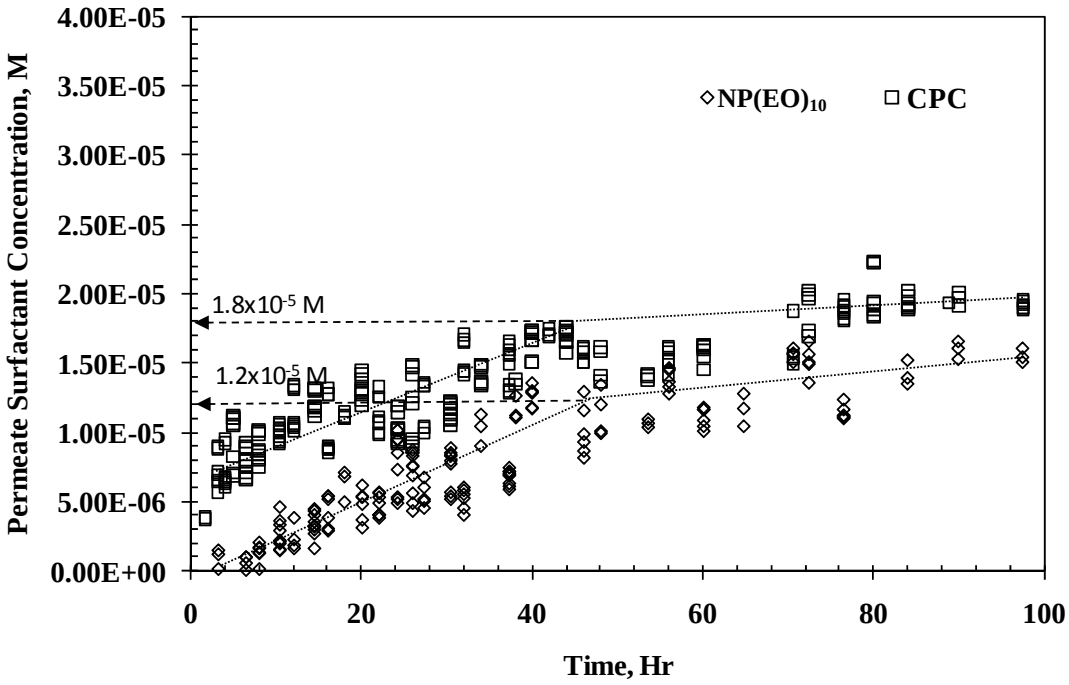

Figure 3.4 Kinetic results for permeate surfactant concentration from SED experiment at 75/25 initial CPC/$NP(EO)_{10}$ mole fraction, 0.2 M NaCl and 30^{o}C. Initial total surfactant concentration in retentate is $3.0x10^{-4}$ M (ten times the mixed CMC of this system).

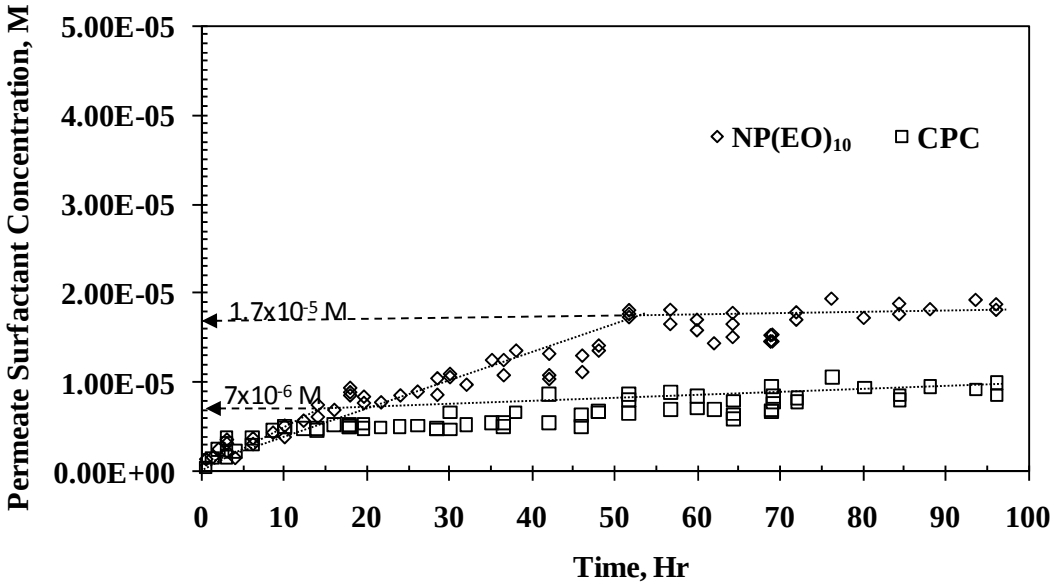

Figure 3.5 Kinetic results for permeate surfactant concentration from SED experiment at 50/50 initial CPC/$NP(EO)_{10}$ mole fraction, 0.2 M NaCl and 30^{o}C. Initial total surfactant concentration in retentate is $2.6x10^{-4}$ M (ten times the mixed CMC of this system).

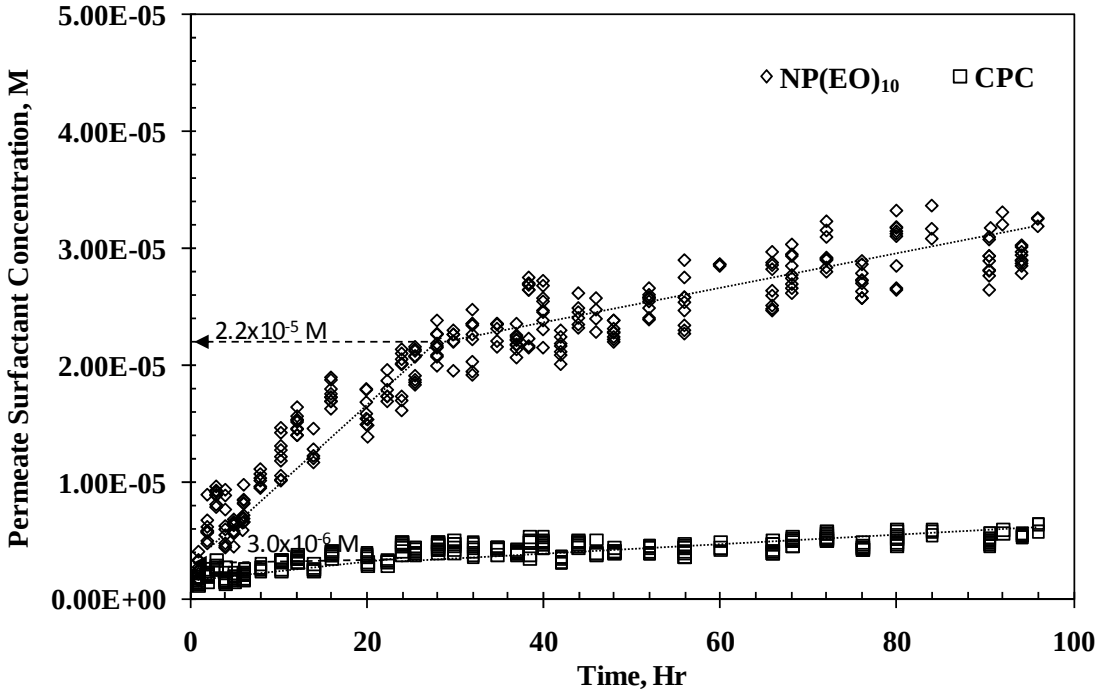

Figure 3.6 Kinetic results for permeate surfactant concentration from SED experiment at 25/75 initial CPC/$NP(EO)_{10}$ mole fraction, 0.2 M NaCl and 30^{o}C. Initial total surfactant concentration in retentate is $2.5x10^{-4}$ M (ten times the mixed CMC of this system).

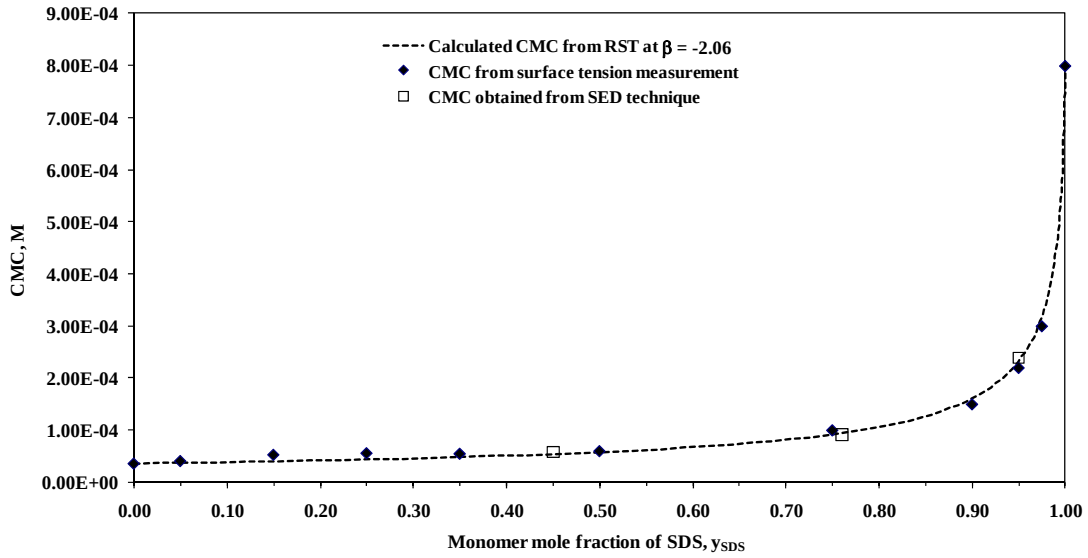

Figure 3.7 CMC of SDS/NP(EO)$_{10}$ mixture at 0.2 M NaCl and 30^{o}C.

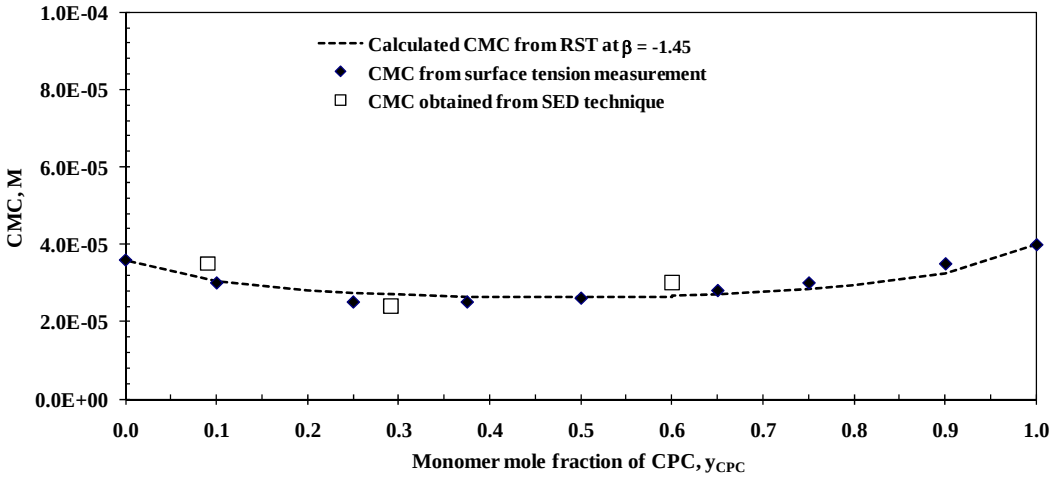

Figure 3.8 CMC of CPC/$NP(EO)_{10}$ mixture at 0.2 M NaCl and 30^{o}C.

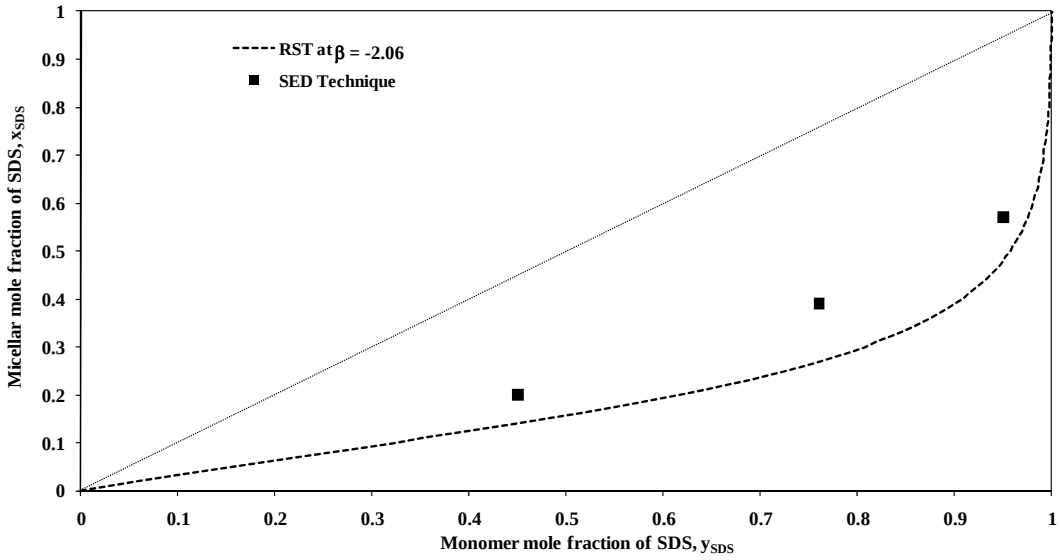

Figure 3.9 Monomer-micelle equilibrium for SDS/NP(EO)$_{10}$ systems at 0.2 M NaCl and 30^{o}C.

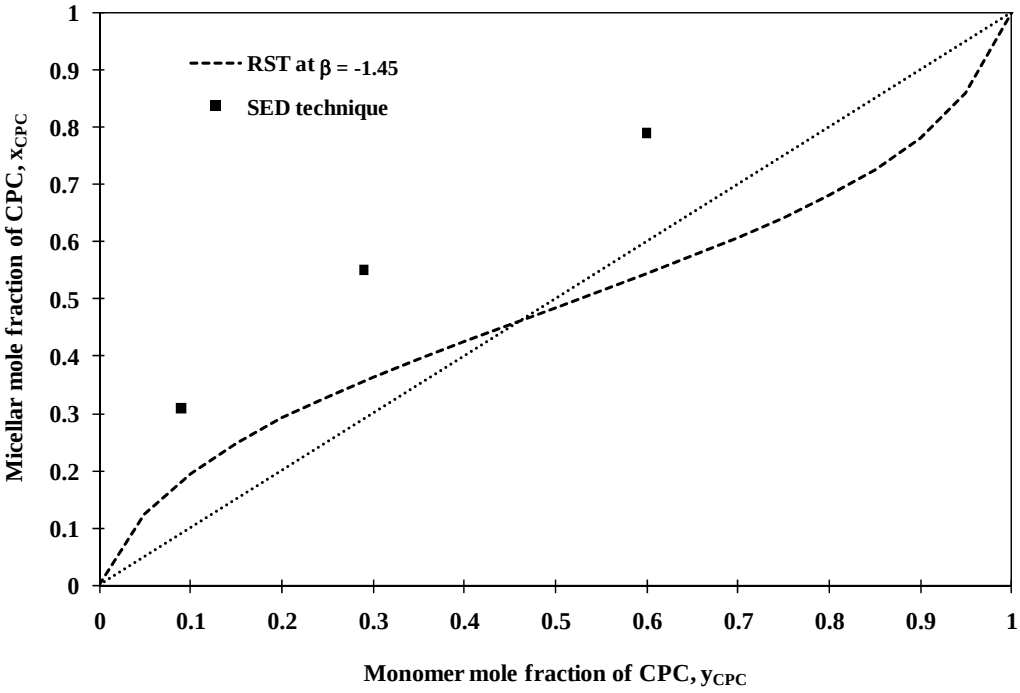

Figure 3.10 Monomer-micelle equilibrium for CPC/$NP(EO)_{10}$ systems at 0.2 M NaCl and 30^{o}C.

Table 3.1 Monomer and micelle compositions of the studied SDS/$NP(EO)_{10}$ systems.

	75/25 initial SDS/$NP(EO)_{10}$ ratio	50/50 initial SDS/$NP(EO)_{10}$ ratio	25/75 initial SDS/$NP(EO)_{10}$ ratio
Initial total surfactant concentration, M	$1x10^{-3}$	$6x10^{-4}$	$5.6x10^{-4}$
Equilibration time for SDS, Hours	8	8	9
Equilibration time for $NP(EO)_{10}$, Hours	2	12	10
Monomer[a]			
Concentration of SDS, M	$2.25x10^{-4}$	$6.90x10^{-5}$	$2.60x10^{-5}$
Concentration of $NP(EO)_{10}$, M	$1.25x10^{-5}$	$2.20x10^{-5}$	$3.20x10^{-5}$
Mixed CMC, M	$2.38x10^{-4}$	$9.10x10^{-5}$	$5.80x10^{-5}$
Mole fraction of SDS	0.95	0.76	0.45
Mole fraction of $NP(EO)_{10}$	0.05	0.24	0.55
Micelle[b]			
Concentration of SDS, M	$3.00x10^{-4}$	$1.62x10^{-4}$	$8.80x10^{-5}$
Concentration of $NP(EO)_{10}$, M	$2.25x10^{-4}$	$2.56x10^{-4}$	$3.56x10^{-4}$
Mole fraction of SDS	0.57	0.39	0.20
Mole fraction of $NP(EO)_{10}$	0.43	0.61	0.80

[a] measured from SED experiments

[b] calculated from mass balance

Table 3.2 Monomer and micelle compositions of the studied CPC/$NP(EO)_{10}$ systems.

	75/25 initial CPC/$NP(EO)_{10}$ ratio	50/50 initial CPC/$NP(EO)_{10}$ ratio	25/75 initial CPC/$NP(EO)_{10}$ ratio
Initial total surfactant concentration, M	$3.0x10^{-4}$	$2.6x10^{-4}$	$2.5x10^{-4}$
Equilibration time for CPC, Hours	44	15	22
Equilibration time for $NP(EO)_{10}$, Hours	46	54	26
Monomer[a]			
Concentration of CPC, M	$1.80x10^{-5}$	$7.00x10^{-6}$	$3.0x10^{-6}$
Concentration of $NP(EO)_{10}$, M	$1.20x10^{-5}$	$1.70x10^{-5}$	$3.2x10^{-5}$
Mixed CMC, M	$3.00x10^{-5}$	$2.40x10^{-5}$	$3.5x10^{-5}$
Mole fraction of CPC	0.60	0.29	0.09
Mole fraction of $NP(EO)_{10}$	0.40	0.71	0.91
Micelle[b]			
Concentration of CPC, M	$1.89x10^{-4}$	$1.16x10^{-4}$	$5.56x10^{-5}$
Concentration of $NP(EO)_{10}$, M	$5.10x10^{-5}$	$9.60x10^{-4}$	$1.24x10^{-4}$
Mole fraction of CPC	0.79	0.55	0.31
Mole fraction of $NP(EO)_{10}$	0.21	0.45	0.69

[a] measured from SED experiments

[b] calculated from mass balance

3.5 REFERENCES

1. Trogus, F. J.; Schechter, R. S.; Wade, W. H. *J. Colloid Interface Sci.* **1979**, *70*, 293.

2. Clint, J. *J. Chem. Soc.* **1975**, *71*, 1327.

3. Hua, X. Y.; Rosen, M. J. *J. Colloid Interface Sci.* **1982**, *90*, 212.

4. Harwell, J. H.; Hoskins, J. C.; Schechter, R. S., Wade, W. H. *Langmuir* **1985**, *1*, 251.

5. Rathman, J.; Scamehorn, J. F. *Langmuir* **1989**, *3*, 372.

6. Sepulveda, L.; Cabrera, W. *J. Colloid Interface Sci.* **1989**, *131*, 8.

7. Cantu, L.; Corti, M.; Degiorgio, V. *J. Phys. Chem.* **1990**, *94*, 793.

8. Huang, L.; Somasundaran, P. *Langmuir* **1996**, *12*, 5790.

9. Ciccarelli, D.; Costantino, L.; D'Errico, G.; Paduano, L.; Vitagliano, V. *Langmuir* **1998**, *14*, 7130.

10. Eads, C. D.; Robosky, L. C. *Langmuir* **1999**, *15*, 2661.

11. Peyre, V. *Langmuir* **2002**, *18*, 1014.

12. Penfold, J.; Staples, E.; Tucker, I.; Thomas, R. K. *Langmuir* **2004**, *20*, 1269.

13. Hierrezuelo, J. M.; Aguiar, J.; Ruiz, C. C. *Colloids Surf., A* **2005**, *264*, 29.

14. Imamura, H.; Tsuchiya, K.; Kondo, Y.; Yoshino, N.; Ohkubo, T.; Sakai, H.; Abe, M. *J. Oleo Sci.* **2005**, *54*, 125.

15. Penfold, J.; Thomas, R.K.; Dong, C.C.; Tucker, I.; Metcalfe, K.; Golding, S.; Grillo, I. *Langmuir* **2007**, *23*, 10140.

16. Barry, B. W.; Russell, G. F. *J. Pharm. Pharmacol.* **1971**, *23*, 241.

17. Kamrath, R. F.; Franses, E. I. *J. Phys. Chem.* **1984**, *88*, 1642.

18. Turner, D.; Gracie, K.; Taylor, T.; Palepu, R. *J. Colloid Interface Sci.* **1998**, *202*, 359.

19. Nishikido, N.; Moroi, Y.; Matuura, R. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1387.

20. Warr, G.; Grieser, F.; Healey, T. W. *J. Phys. Chem.* **1983**, *87*, 1220.

21. Rathman, J. F.; Christian, S. D. *Langmuir* **1990**, *6*, 391.

22. Smirnova, N. A. *Fluid Phase Equilib.* **1995**, *110*, 1.

23. Goloub, T. P.; Pugh, R. J.; Zhmud, B. V. *J. Colloid Interface Sci.* **2000**, *229*, 72.

24. Asakawa, T.; Johten, K.; Miyagishi, S.; Nishida, M. *Langmuir* **1985**, *1*, 347.

25. Asakawa, T.; Miyagishi, S.; Nishida, M. *Langmuir* **1987**, *3*, 821.

26. Asakawa, T.; Hisamatsu, H.; MIyagishi, S. *Langmuir* **1995**, *11*, 478.

27. Asakawa, T.; Ishikawa, K.; Miyagishi, S. *J. Colloid Interface Sci.* **2001**, *240*, 365.

28. Davey, T. W.; Warr, G. G.; Asakawa, T. *Langmuir* **2003**, *19*, 5266.

29. Akisada, H. *J. Colloid Interface Sci.* **1984**, *97*, 105.

30. Nguyen, C. M.; Rathman, J. F.; Scamehorn, J. F. *J. Colloid Interface Sci.* **1986**, *112*, 438.

31. Hall, D. G. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3529.

32. Yu, Z. J.; Zhao, G. X. *J. Colloid Interface Sci.* **1993**, *156*, 325.

33. Akbas, H.; Iscan, M.; Sidim, T. *J. Surfactants Deterg.* **2000**, *3*, 77.

34. Akisada, H. *J. Colloid Interface Sci.* **2001**, *240*, 323.

35. Maeda, H. *J. Phys. Chem. B* **2005**, *109*, 15933.

36. Holland, P. M.; Rubingh, D.N. *J. Phys. Chem.* **1983**, *87*, 1984.

37. Filipovic-Vincekovic, N.; Juranovic, I.; Grahek, Z. *Colloids Surf., A* **1997**, *125*, 115.

38. Reif, I.; Somasundaran, P. *Langmuir* **1999**, *15*, 3411.

39. Rosen, M. J.; Zhou, Q. *Langmuir* **2001**, *17*, 3532.

40. Li, F.; Rosen, M. J.; Sulthana, S. B. *Langmuir* **2001**, *17*, 1037.

41. Kharitonova, T. V.; Ivanova, N. I.; Summ, B. D. *Colloid J.* **2002**, *64*, 224.

42. Prosser, A. J.; Franses, E. I. *J. Colloid Interface Sci.* **2003**, *263*, 606.

43. Tsubone, K. *J. Colloid Interface Sci.* **2003**, *261*, 524.

44. Sehgal, P.; Doe, H.; Sharma, M. *Colloid Polym. Sci.* **2003**, *282*, 188.

45. Al-Wardian, A.; Glenn, K. M.; Palepu, R. M. *Colloids Surf., A* **2004**, *247*, 115.

46. Kakehashi, R.; Shizuma, M.; Yamamura, S.; Takeda, T. *J. Colloid Interface Sci.* **2004**, *279*, 253.

47. Nakano, T. Y.; Sugihara, G.; Nakashima, T.; Yu, S. C. *Langmuir* **2002**, *18*, 8777.

48. Motomura, K.; Yamanku, M.; Aratono, M. *Colloid Polym. Sci.* **1984**, *262*, 948.

49. Nagarajan, R. *Langmuir* **1985**, *1*, 331.

50. Puvvada, S.; Blankschtein, D. *Langmuir* **1990**, *6*, 894.

51. Puvvada, S.; Blankschtein, D. *J. Phy. Chem.* **1992**, *96*, 5567.

52. Puvvada, S.; Blankschtein, D. *J. Phy. Chem.* **1992**, *96*, 5579.

53. Sarmoria, C.; Puvvada, S.; Blankschtein, D. *Langmuir* **1992**, *8*, 2690.

54. Lue, L.; Blankschtein, D. *J. Chem. Phys.* **1995**, *103*, 1229.

55. Zoeller, N. J.; Blankschtein, D. *Ind. Eng. Chem. Res.* **1995**, *34*, 4150.

56. Shiloach, A.; Blankschtein, D. *Langmuir* **1997**, *13*, 3968.

57. Blankschtein, D.; Shiloach, A.; Zoeller, N. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 294.

58. Rosen, M. J. *Surfactants and Interfacial Phenomena*, 3rd ed.; Wiley: New York, 2004; Chapter 11.

59. Ellott, J.R.; Lira, C.T. *Introductory Chemical Engineering Thermodynamics*; Prentice Hall: New Jersey, 1999, p 364-366.

60. Nishikido, N. *J. Colloid Interface Sci.* **1977**, *60*, 242.

61. Lohateeraparp, P.; Scamehorn, J. F.; Sabatini D. A. *Langmuir*, submitted.

62. Hall, D. G. *J. Chem. Soc., Faraday Trans.* **1981**, *77*, 1121.

63. Evans, D. F.; Mitchel, D. J.; Ninham, B. W. *J. Phys. Chem.* **1984**, *88*, 6344.

64. Hayter, J. B. *Langmuir* **1992**, *8*, 2873.

65. Maeda, H. *J. Colloid Interface Sci.* **2001**, *241*, 18.

66. Maeda, H. *J. Colloid Interface Sci.* **2003**, *258*, 390.

67. Bansal, V.; Biswas, A.; Balusubramanian, D. *Colloid Polym. Sci.* **1979**, *257*, 1083.

68. de Weerd, R.; de Haan, J.; van de Ven, L.; Buck, H. *J. Phys. Chem.* **1982**, *86*, 2528.

69. Kamrath, R. F.; Franses, E. I. *Ind. Eng. Chem. Fundam.* **1983**, *22*, 230.

70. Haque, M. E.; Das, A. R.; Rakshit, A. K.; Moulik, S. P. *Langmuir* **1996**, *12*, 4084.

71. Hines, J. D.; Thomas, R. K.; Garrett, P. R.; Rennie, G. K.; Penfold, J. *J. Phys. Chem. B* **1997**, *101*, 9215.

72. Lohateeraparp, P.; Scamehorn, J. F.; Sabatini, D. A. *Langmuir*, submitted.

73. Scamehorn, J. F.; Sabatini, D. A.; Harwell, J. H. In *Encyclopedia of Supramolecular Chemistry*, Atwood, J.; Stead, J., Eds; Marcel Dekker, New York, 2004; p 1458-1469.

74. Rosen, M. J. *Surfactants and Interfacial Phenomena*, 3rd ed.; Wiley, New York, 2004; Chapter 3.

75. Smith, G. A.; Christian, S. D.; Tucker, E. E.; Scamehorn, J. F. *J. Solution Chem.* **1986**, *15*, 519.

CHAPTER 4

Measuring Monomer-Micelle Equilibrium by Using Semi-Equilibrium Dialysis. III. Excess Enthalpies and Entropies of Mixed Micelle Formation for Binary Surfactant Systems

The semi-equilibrium dialysis (SED) technique is used here to measure monomer-micelle equilibrium for ionic/nonionic surfactant mixtures at different temperatures to permit calculation of excess Gibbs free energy (G^E), excess enthalpy (H^E) and excess entropy (S^E) of mixed micelle formation. The values of the mixed CMC and G^E from the SED technique measured here agree with those from surface tension measurements and those predicted from regular solution theory (RST). However, predictions of H^E and S^E from RST are in gross disagreement with those from SED experiments.

4.1 INTRODUCTION

Regular solution theory (RST) has been commonly used in the last few decades to predict monomer-micelle equilibrium[1-8] by using simple equations with only one adjustable interaction parameter (β) as described in Part II of this series[9]. The simplicity of RST and its ability to describe CMC data has led to its popularity. The CMC is easy to measure and is often the only parameter available for a mixed surfactant system. However, the value of β can depend on surfactant composition instead of being invariant. For example, when surfactant composition is varied, the excess free energy of mixing resulting from mixed micelle formation can be unsymmetrical[10], in contrast to the symmetrical prediction resulting from RST. In Part II of this series[9], the monomer-micelle equilibrium of two binary surfactant mixtures were measured by the SED technique at 30^{o}C. At a given monomer composition, the predicted micelle composition from RST was shown to differ greatly from the experimental data even though CMC data were well correlated by RST.

The heat of mixing on mixed micelle formation as measured by calorimetry has been shown to deviate from RST predictions[11-14]. In some cases, measured heats are endothermic whereas RST predicted exothermic mixing. From CMC data and calorimetric measurements, the calculated excess entropy of mixing for mixed micelle formation can be large, rather than zero as assumed by RST[15]. Another consequence of enthalpic and entropic assumptions behind RST being in error is that βRT (where R is the gas constant and T is temperature) is observed to depend on temperature for a particular surfactant mixture[16-21] while RST predicts temperature independence.

In this Part III of the series, the same binary surfactant mixtures studied in Part II[9] is studied at different temperatures and the SED results used to calculate excess Gibbs free energy, excess enthalpy, and excess entropy of mixed micelle formation with the results compared to RST predictions.

4.2 EXPERIMENTAL SECTION

4.2.1 Materials

The source and purification of materials were described in Part I[22]. The studied surfactants were sodium dodecyl sulfate (SDS), cetylpyridinium chloride (CPC), and nonylphenol polyethoxylate with an average degree of polymerization of 10 ($NP(EO)_{10}$). The salt used in this study was sodium chloride (NaCl).

4.2.2 Methods

Experimental methods were described in Part I[22] and Part II[9] of this series. The two studied surfactant mixtures were SDS/$NP(EO)_{10}$ and CPC/$NP(EO)_{10}$. In this paper, the SED experiment was conducted at two different temperatures, 40^{o}C and 50^{o}C, using the same conditions used in Part II at 30^{o}C. The initial total surfactant concentration in the retentate compartment was ten times the mixed CMC of studied systems. Both permeate and retentate compartments initially contained 0.2 M NaCl.

4.3 THEORY

In this section, we discuss how the SED data can be used to calculate the excess Gibbs free energy of mixed micelle formation (G^E), excess enthalpy of mixed micelle formation (H^E), and excess entropy of mixed micelle formation (S^E). Subsequently, we discuss how these thermodynamic parameters can be estimated from RST.

The standard state for the monomer is defined as 1 M (hypothetical since monomer cannot attain this concentration) and the standard state for the surfactant in the micelle is the pure component micelle, both at the same added electrolyte level as for the mixed surfactant system (0.2 M NaCl in this study). Equating the partial fugacity of a surfactant component in the monomer and in the mixed micelle[23]:

$$\gamma_i^M = \frac{y_i C_{12}}{x_i C_i^0} \tag{1}$$

where γ_i^M is the activity coefficient of surfactant i in the micelle, y_i is the monomer mole fraction of surfactant i, x_i is the mole fraction of surfactant i in the mixed micelle, C_i^0 is the CMC of surfactant i, and C_{12} is the CMC of the mixed surfactant system.

The excess partial molar Gibbs free energy of surfactant i ($\overline{G_i^E}$) in the mixed micelle is related to the activity coefficient by[24]:

$$\overline{G_i^E} = RT \ln \gamma_i^M \tag{2}$$

Where R is the gas constant and T is temperature. The specific excess Gibbs free energy of mixed micelle formation (G^E) is[24]:

$$G^E = \sum_{i=1}^{n} (x_i \overline{G_i^E}) = RT \sum_{i=1}^{n} (x_i \ln (\frac{y_i C_{12}}{x_i C_i^0})) \quad (3)$$

The specific excess enthalpy (H^E) and specific excess entropy (S^E) of mixed micelle formation can be calculated[25] from the temperature dependence of G^E:

$$\frac{\partial G^E}{\partial T} = -S^E \quad (4)$$

$$H^E = G^E + T S^E \quad (5)$$

While here we only consider binary surfactant systems, since these were studied in this work, extension to additional components is straightforward[23]. Substituting SED data for composition and concentration of surfactant i in monomer and in micelle into equations 1-3 permits calculation of G^E at a given micelle composition (x_1, x_2). At this composition, the temperature dependence of G^E permits calculation of S^E and H^E from equations 4 and 5. Since SED data is not at exactly the same micelle composition at different temperatures, some interpolation of the SED data is necessary between different compositions at a given temperature.

RST assumes that all of the nonideality of mixing is due to deviation of the enthalpy of mixing from ideal mixing. For a binary system[26]:

$$(H^E)_{RST} = x_1 x_2 \beta RT \quad (6)$$

$$(S^E)_{RST} = 0 \quad (7)$$

Where β is the dimensionless interaction parameter obtained from CMC data for the systems studied here in Part II of this series[9]. Micellar activity coefficients are related to β by[23,27]:

$$(\gamma_1^M)_{RST} = e^{(\beta x_2^2)} \quad (8)$$

$$(\gamma_2^M)_{RST} = e^{(\beta x_1^2)} \quad (9)$$

Combining equations 5 -7 yields:

$$(G^E)_{RST} = x_1 x_2 \beta RT \quad (10)$$

4.4 RESULTS AND DISCUSSION

4.4.1 CMC Determination and β Parameter Calculation

Surface tensions of surfactant solutions were measured at 40°C and 50°C. The values were plotted as a function of total surfactant concentration. The CMC is determined as the point where a sharp transition to a minimum in surface tension occurs[28].

The β parameter at each surfactant mixture ratio was calculated from the measured CMC values as described in Part II [9] of this series at 30°C. As presented further below, the average β parameters of the SDS/NP(EO)$_{10}$ system at 30°C, 40°C, and 50°C are -2.06, -1.94 and -1.65, respectively. For the CPC/NP(EO)$_{10}$ mixture, the average β values are -1.45, -1.99, and -1.16, respectively.

4.4.2 Comparing SDS/NP(EO)$_{10}$ SED Results to RST Predictions

The SED experiments were conducted at three SDS/NP(EO)$_{10}$ surfactant ratios (75/25, 50/50 and 25/75) and two different temperatures (40^{o}C and 50^{o}C) to determine the permeate surfactant component concentrations at different contact times. Analogous data at 30^{o}C from Part II[9] of this series is combined with these results in temperature dependence calculations.

Figs. 4.1 and 4.2 show the CMC as a function of SDS monomer mole fraction (y_{SDS}) at 40^{o}C and 50^{o}C. They show a comparison of the CMC values from surface tension measurements, the SED experiments, and RST predictions based on the average β parameter from surface tension measurements. The CMC values obtained from surface tension measurements and the SED method agree well with each other and are well correlated by the predictions from RST at both studied temperatures; this agreement was also found in Part II[9] at 30^{o}C.

Figs. 4.3 and 4.4 show the SDS micellar mole fraction (x_{SDS}) vs. SDS monomer mole fraction (y_{SDS}), at 40^{o}C and 50^{o}C, respectively. From the RST predictions (dashed line), there is no azeotrope (where $x_{SDS} = y_{SDS}$) and x_{SDS} is always less than y_{SDS}. The measured x_{SDS} from the SED technique is consistently higher than the values predicted by RST; the difference between the measured x_{SDS} and predicted values are between 17% and 32% at 40^{o}C and between 20% and 72% at 50^{o}C. The differences are in the same range as the deviation reported[9] at 30^{o}C.

4.4.3 Comparing CPC/NP(EO)$_{10}$ SED Results to RST Predictions

The SED experiments were conducted at five CPC/$NP(EO)_{10}$ surfactant ratios at 40°C (at 90/10, 75/25, 50/50, 25/75 and 10/90 ratios) and at four ratios at 50°C (at 10/90, 35/65, 50/50 and 75/25 ratios) to determine the permeate surfactant component concentrations at different contact times. Analogous data at 30°C from Part II[9] of this series is combined with these results in temperature dependence calculations.

Figs. 4.5 and 4.6 show the CMC as a function of CPC monomer mole fraction (y_{CPC}) at 40°C and 50°C based on surface tension measurements, the SED experiments, and RST predictions based on the average β parameter from surface tension measurements. The CMC values obtained from surface tension measurements and the SED method agree well with each other and are well correlated by the predictions from RST at both studied temperatures; this agreement was also found in Part II[9] at 30°C.

The monomer-micelle equilibrium compositions at 40°C and 50°C from the RST predictions and the SED technique are compared in Figs. 4.7 and 4.8, respectively. In Fig. 4.7 (at 40°C), RST predicts an azeotrope at $y_{CPC} = x_{CPC} = 0.54$. At lower CPC mole fraction, RST predicts that the micelle is enriched in CPC compared to the monomer and at higher CPC mole fractions, the micelles are enriched in the $NP(EO)_{10}$ compared to the monomer. The azeotrope from SED measurements is at $y_{CPC} = x_{CPC} = 0.25$ (Fig. 4.7), substantially lower than the prediction from RST. The difference between the measured values of x_{CPC} and those predicted from RST is between 22% and 85%. At 50°C, the azeotrope estimated from the SED experiment is approximately at $y_{CPC} = 0.35$, lower than the RST predictions (azeotrope at $y_{CPC} = 0.68$). The difference between the experimental measurement and the RST predictions of x_{CPC} is in the range of 12 – 86%. At lower CPC mole fractions than the azeotrope at both 40°C and 50°C, RST predicts that micelles are preferentially enriched in CPC relative to

monomer, whereas the experimental data shows the opposite. This deviation between the measured and RST predicted values of x_{CPC} at 40°C and 50°C for the CPC/NP(EO)$_{10}$ mixture is greater than that at 30°C reported in Part II[9].

A comparison of monomer-micelle equilibrium composition from the SED technique and the RST prediction in Part II[9] and this paper show that although the RST can predict the CMC values well, the monomer-micelle compositions predicted by the RST can be in gross error and can even be contradictory in trend (ionic surfactant-rich micelle vs. non-ionic surfactant-rich micelle) from the experimental measurements.

4.4.4 Comparing Excess Properties from SED Results to RST Predictions

Excess enthalpy (H^E), excess entropy (S^E) and excess Gibbs free energy (G^E) of mixing for the SDS/NP(EO)$_{10}$ and the CPC/NP(EO)$_{10}$ mixtures at different studied temperatures were calculated based on the experimental results from the SED technique using equations 1-5. These calculated values were compared to the predictions from the RST from equations 6, 7, and 10.

The SED-based calculated and RST predicted values of H^E, S^E and G^E for SDS/NP(EO)$_{10}$ mixtures at 30°C, 40°C and 50°C are plotted in Figs. 4.9 through 4.11, respectively. The values of H^E, TS^E and G^E for SDS/NP(EO)$_{10}$ mixture vary slightly at different temperatures. The value of G^E from SED data is directly related to the mixture CMC, so is well described by RST at all three temperatures. However, the SED values of H^E and S^E considerably deviate from RST predictions: RST predicts minimum H^E values of -1,298 J/mol, -1,262 J/mol and – 1,108 J/mol at 30°C, 40°C and 50°C, respectively, while the minimum in the values of H^E calculated from the SED results is in the range of -3800 J/mol to -3900 J/mol. The H^E values of SDS/NP(EO)$_{10}$

mixtures from the SED technique compares favorably to the calorimetric results[29] for the same studied system (except for different salinities). The difference in H^E values from these two experimental techniques could be due to different added salt concentrations (0.03 M and 0.2 M, respectively) as the heat of mixing in mixed micelle formation is strongly dependent on electrostatic interactions[29]. The S^E values calculated from the SED data deviate from zero as predicted by RST. This observation is consistent with previous literature[15] and it indicates that the RST assumption of zero excess entropy during mixed micelle formation is invalid. For all studied temperatures, the calculated SED values of H^E and S^E do not show the symmetry with respect to micellar mole fraction predicted by RST. Furthermore, the experimental value of βRT is not constant at different temperatures (-5192 J/mol at 30°C, -5051 J/mol at 40°C, and -4433 J/mol at 50°C) as is hypothesized by RST.

Figs. 4.12 to 4.14 show the values of H^E, TS^E and G^E calculated from SED data for the CPC/$NP(EO)_{10}$ system at 30°C, 40°C and 50°C, respectively, and corresponding predictions from RST. For this mixture, the G^E values calculated from the SED experimental results compare well to predictions from RST. The minimum values of H^E from the SED data is lower than -10,000 J/mol, about an order of magnitude greater than the RST predictions (-913 J/mol at 30°C, -1,295 J/mol at 40°C, and -779 J/mol at 50°C). These H^E values from SED experiment are almost one order of magnitude lower than those measured by calorimetry for the CPC/$NP(EO)_{10}$[29]. The significant higher salt concentration used in this study could cause this difference. This work demonstrates that S^E deviates greatly from zero, again invalidating RST assumptions for this system. Although the minimum of H^E and S^E for CPC/$NP(EO)_{10}$ is predicted from RST to be at $x_{CPC} = 0.5$, the experimental H^E and S^E curves are unsymmetrical at

all three studied temperatures and the values of βRT from experiment vary with temperature (-3655 J/mol at 30°C, -5181 J/mol at 40°C, and -3117 J/mol at 50°C). These observations are all inconsistent with RST predictions.

From Figs. 4.9-4.14, the values of H^E and S^E are positive at the lowest mole fraction of the ionic surfactant studied for both SDS/$NP(EO)_{10}$ and CPC/$NP(EO)_{10}$ even though both parameters are predicted to be negative by RST. Thus, endothermic mixing is observed experimentally whereas RST predicts exothermic mixing. And a more disordered mixed micelle is observed than predicted by ideal mixing, whereas at other compositions, a more ordered system is observed. From Figs. 4.7 and 4.8, this composition corresponds to the greatest deviation between experimental micelle compositions and those predicted by RST; the micelle is greatly enriched in the ionic surfactant at this monomer composition.

Random mixing (ideal entropy of mixing) is assumed in RST. This is not a reasonable assumption for ionic and nonionic head groups since it is reduction of electrostatic repulsion between charged head groups due to insertion of nonionic head groups between them that is responsible for synergism (negative β values) in mixed ionic/nonionic micelles. A macroscopic model[30] which accounts for the reduction in the absolute value of the electrostatic potential at the micelle surface due to the nonionic surfactant head groups causing the charge density on this surface to decrease can predict the CMC values of ionic/nonionic surfactant systems. Obviously, dissimilar head groups would not be randomly ordered with such forces at work. Models to supplant RST based on fundamental principles are needed to account for this complex interaction between enthalpic and entropic effects and can possibly derive from local composition models from statistical mechanics. However, it is the simplicity of RST

which makes it so attractive whereas molecular thermodynamic models tend to be complex. A tremendous inhibition in development of advanced models has been the lack of a data base of monomer-micelle equilibrium and enthalpies/entropies of mixing for mixed micelle formation. The SED technique is a relatively easy-to-use, inexpensive, universal technique only requiring the analytical ability to measure the concentration of each surfactant component which can now permit development of such a data base for mixed surfactant systems to give a basis for further model development.

4.5 CONCLUSIONS

The SED technique can effectively measure monomer-micelle equilibrium, as demonstrated in this series of papers for an anionic/nonionic and a cationic/nonionic surfactant system. Data from SED as a function of temperature permit calculation of excess enthalpy and entropy for formation of mixed micelles as an alternative to calorimetry. Predicted micelle compositions and excess enthalpy and entropy of micelle formation from RST can be in gross disagreement with experimental data even though CMC values are well-predicted by RST. The H^E and S^E can be very unsymmetical with micelle composition for binary ionic/nonionic surfactant micelles. For example, both H^E and S^E can be either negative or positive depending on composition. The SED technique can permit simple measurement of monomer-micelle equilibrium for practical surfactant mixtures as well as permitting development of a data base to aid development of the next generation of thermodynamic models for mixed micelles.

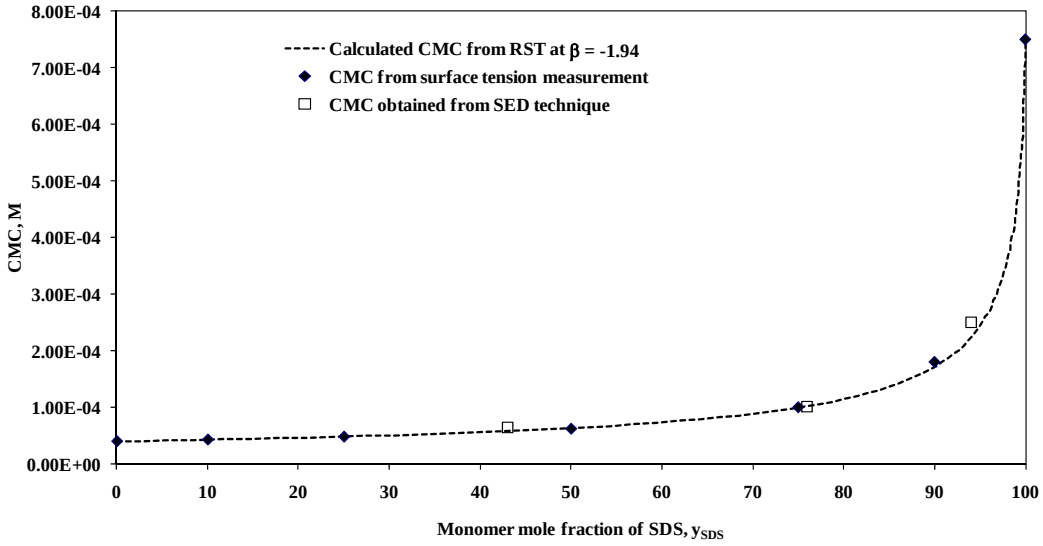

Figure 4.1 CMC of SDS/NP(EO)$_{10}$ mixture at 0.2 M NaCl and 40^{o}C.

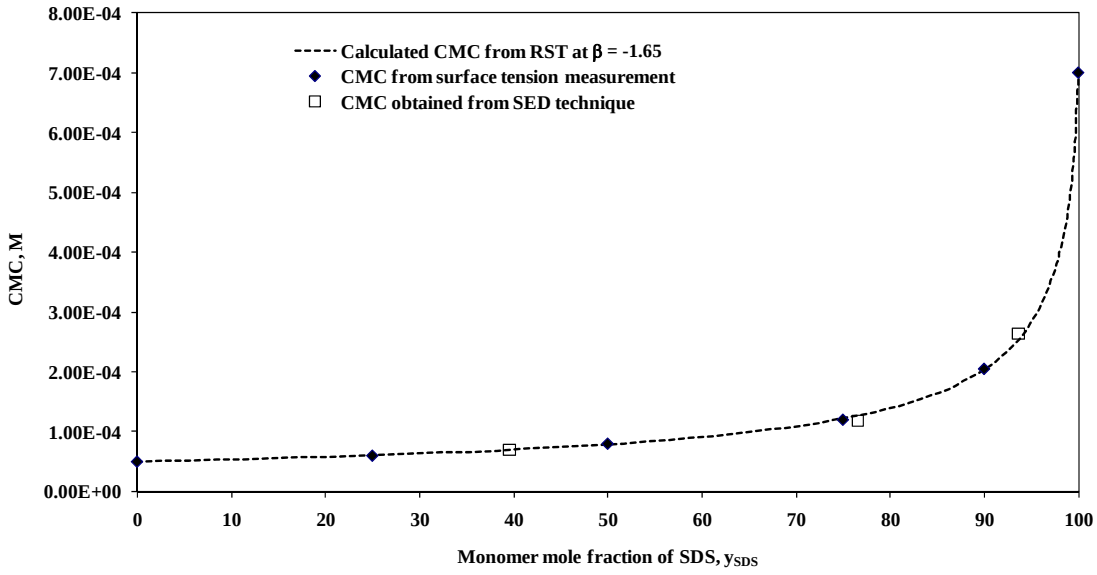

Figure 4.2 CMC of SDS/NP(EO)$_{10}$ mixture at 0.2 M NaCl and 50^{o}C.

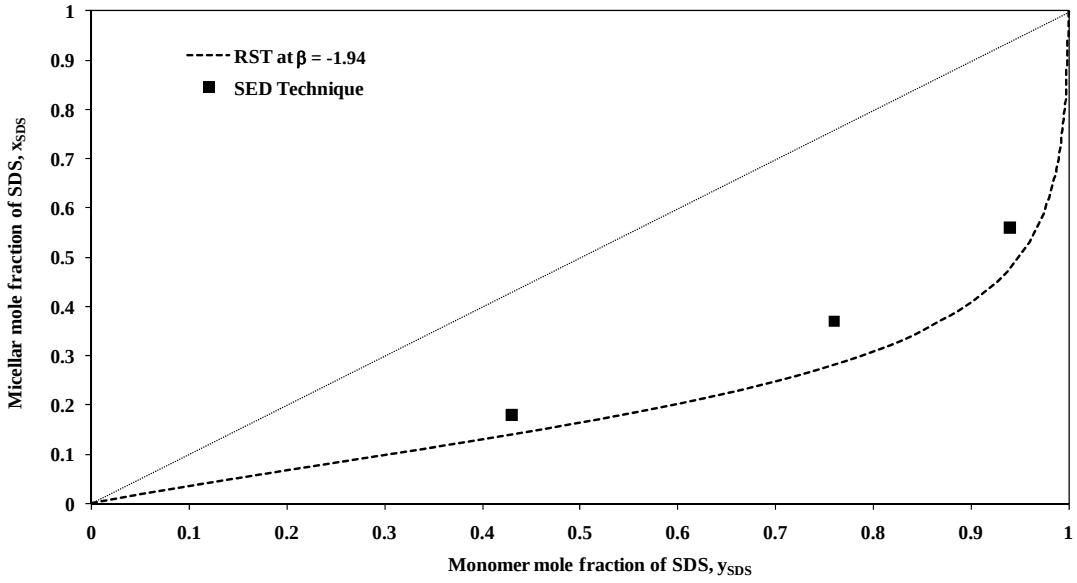

Figure 4.3 Monomer-micelle equilibrium for SDS/NP(EO)$_{10}$ systems at 0.2 M NaCl and 40^{o}C.

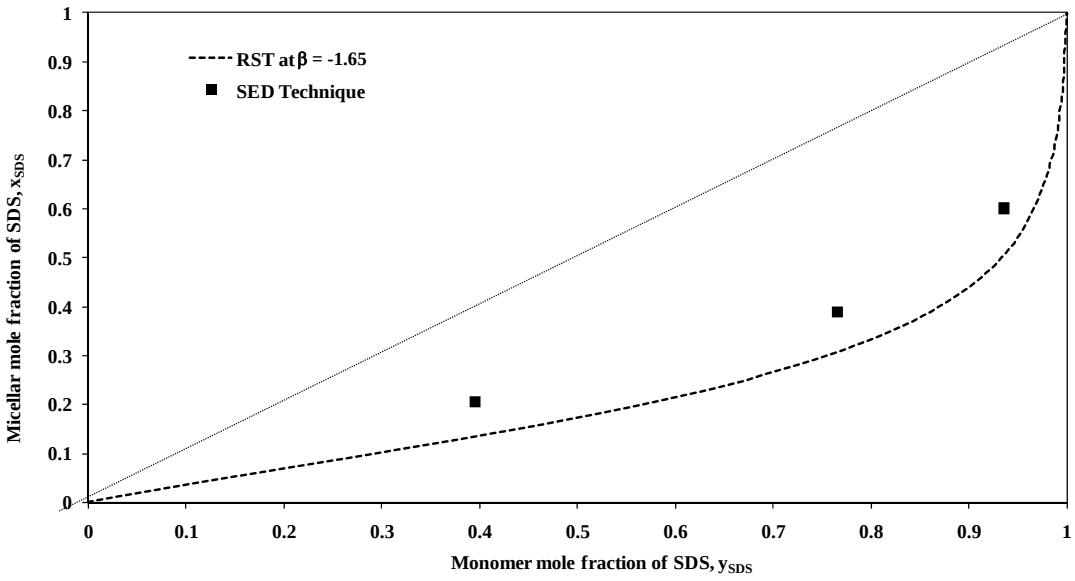

Figure 4.4 Monomer-micelle equilibrium for SDS/NP(EO)$_{10}$ systems at 0.2 M NaCl and 50^{o}C.

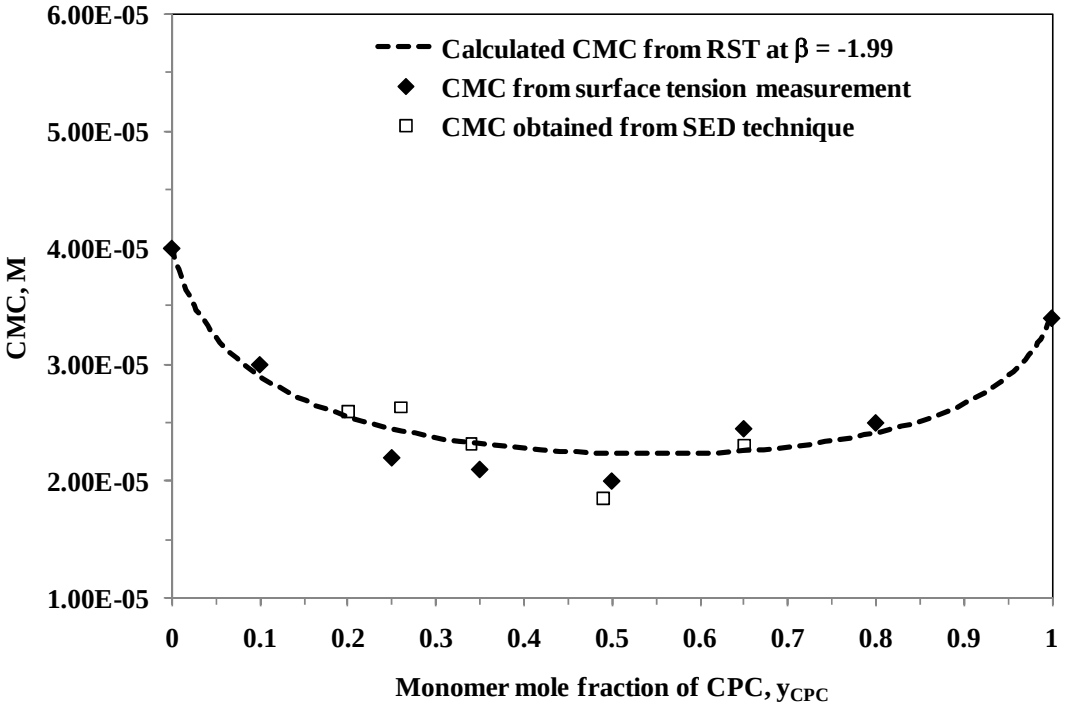

Figure 4.5 CMC of CPC/NP(EO)$_{10}$ mixture at 0.2 M NaCl and 40^{o}C.

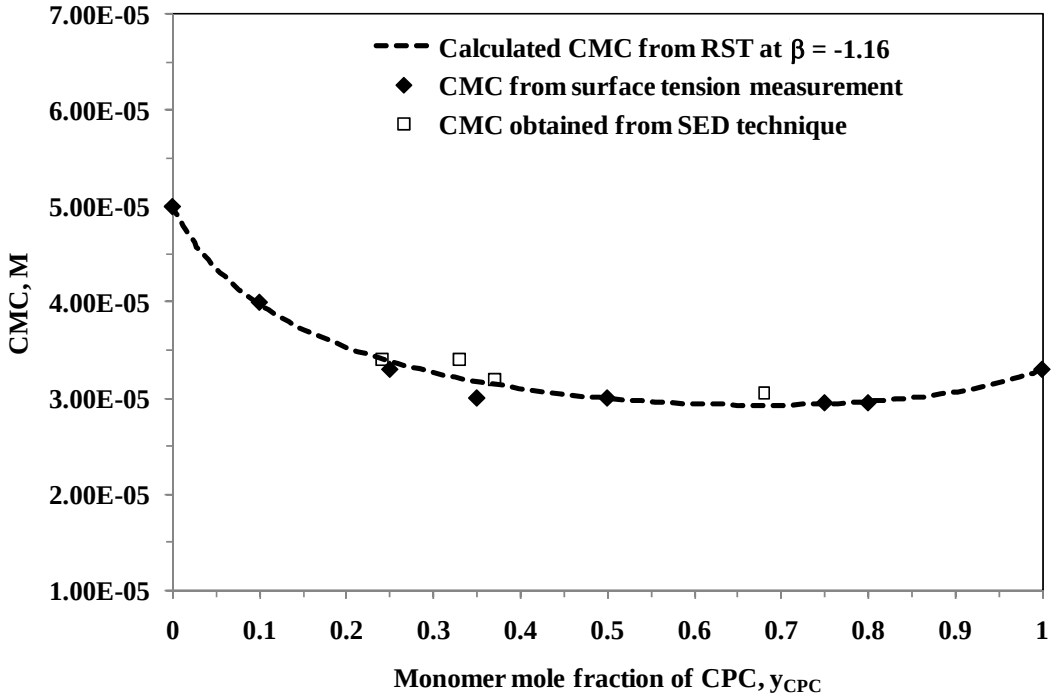

Figure 4.6 CMC of CPC/NP(EO)$_{10}$ mixture at 0.2 M NaCl and 50^{o}C.

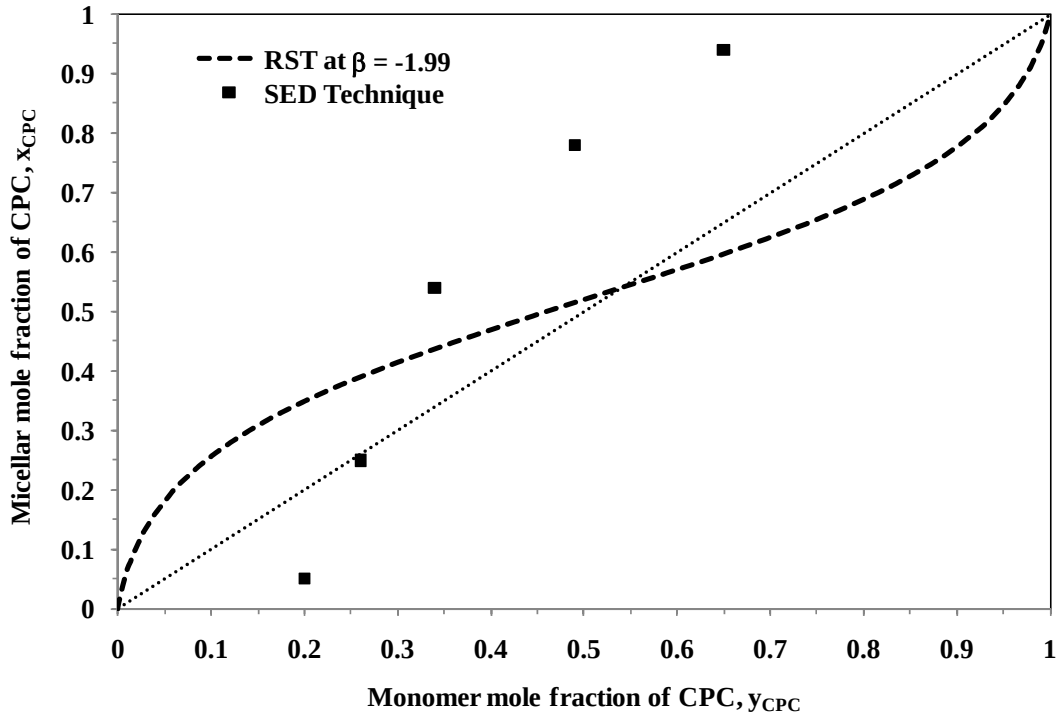

Figure 4.7 Monomer-micelle equilibrium for CPC/$NP(EO)_{10}$ systems at 0.2 M NaCl and 40^{o}C.

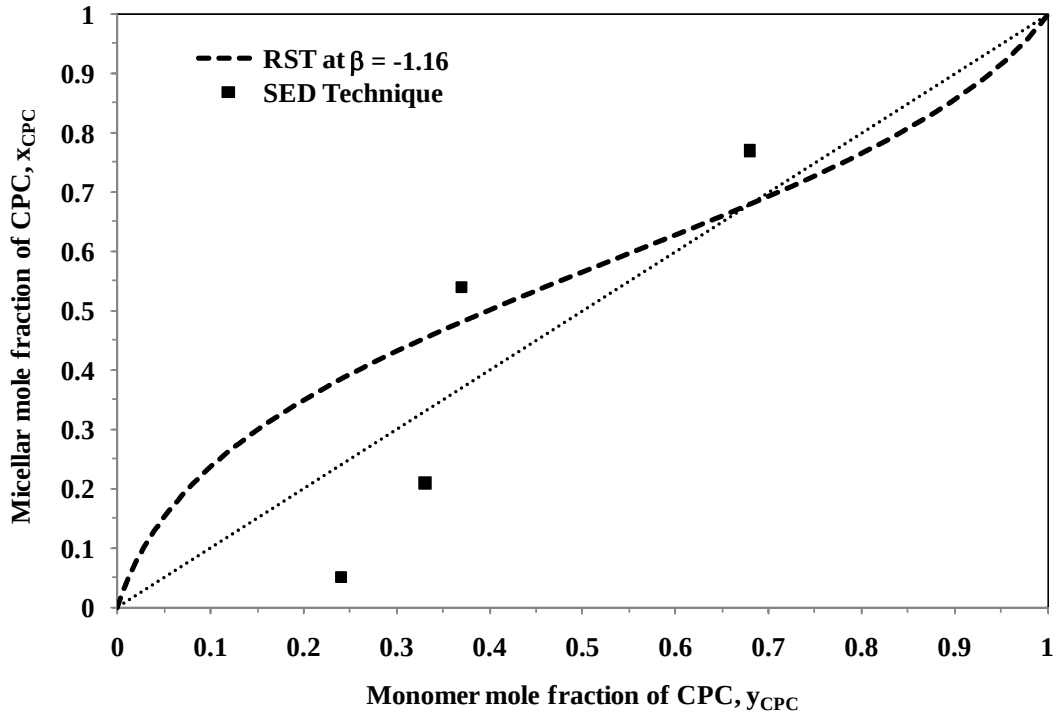

Figure 4.8 Monomer-micelle equilibrium for CPC/$NP(EO)_{10}$ systems at 0.2 M NaCl and 50^{o}C.

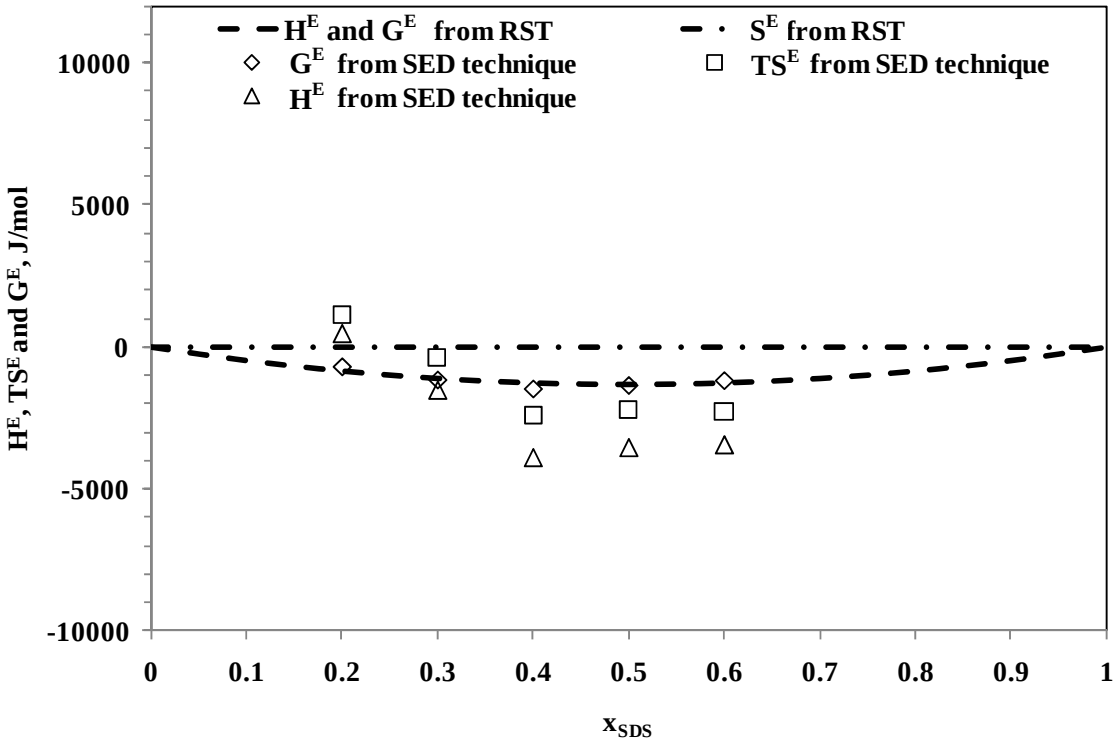

Figure 4.9 Excess enthalpy, excess entropy and excess Gibbs free energy for SDS/NP(EO)$_{10}$ systems at 0.2 M NaCl and 30^{o}C.

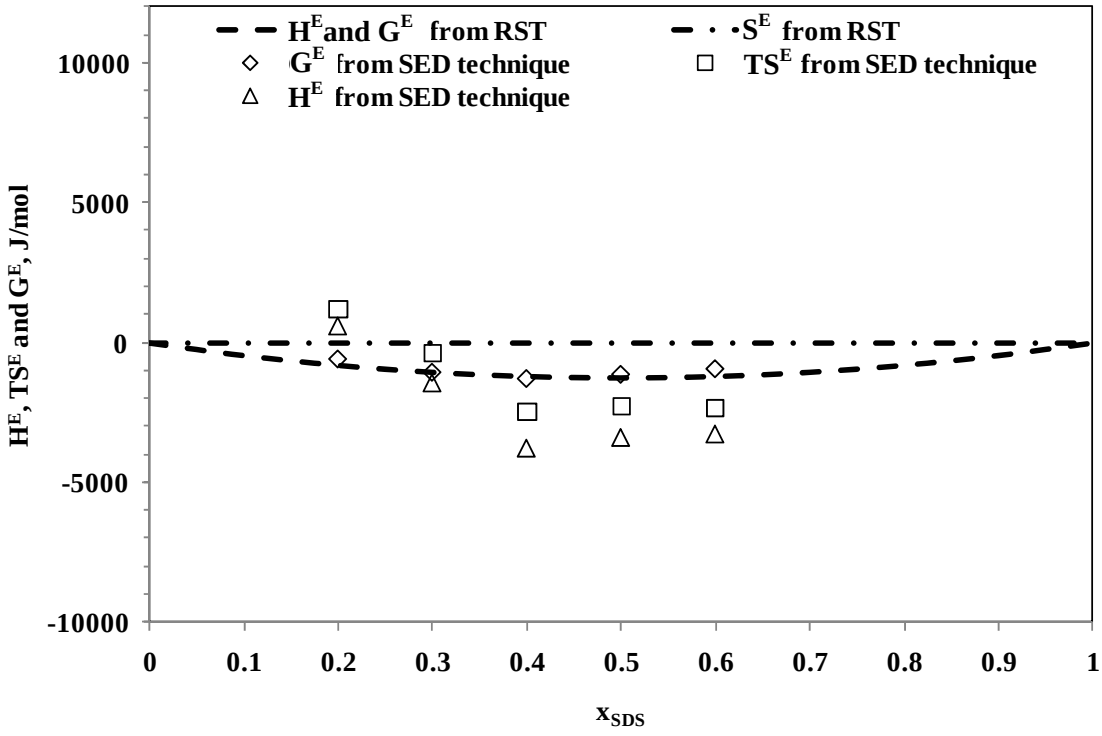

Figure 4.10 Excess enthalpy, excess entropy and excess Gibbs free energy for SDS/NP(EO)$_{10}$ systems at 0.2 M NaCl and 40^{o}C.

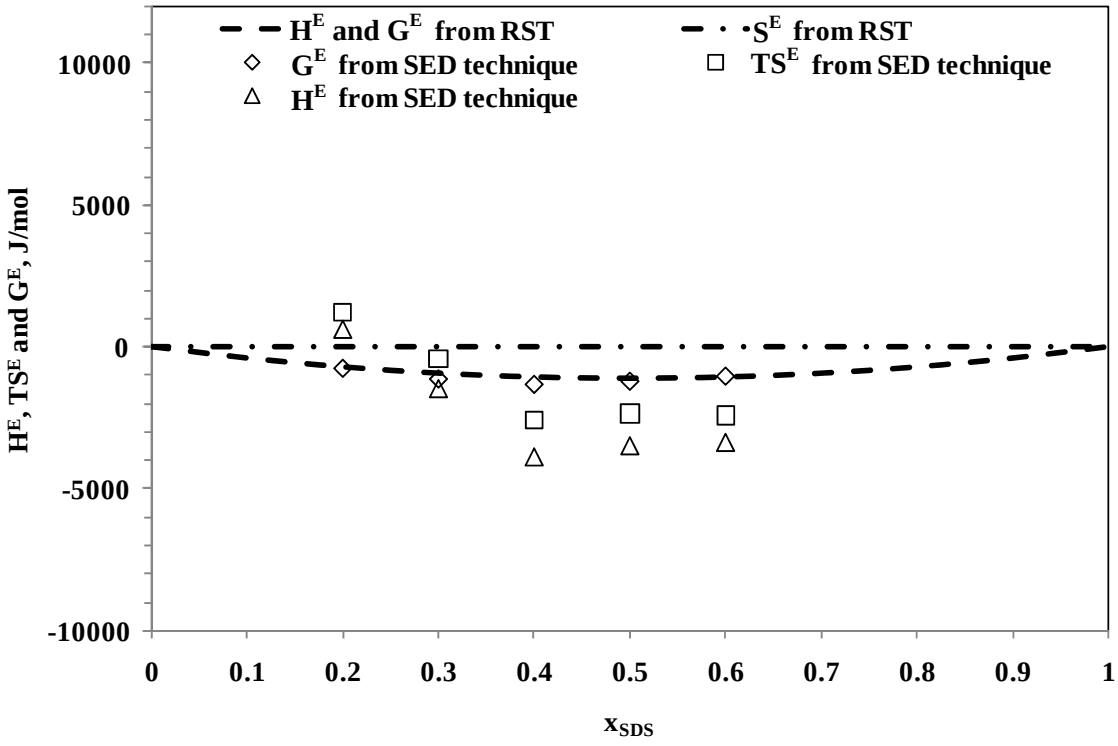

Figure 4.11 Excess enthalpy, excess entropy and excess Gibbs free energy for SDS/NP(EO)$_{10}$ systems at 0.2 M NaCl and 50^{o}C.

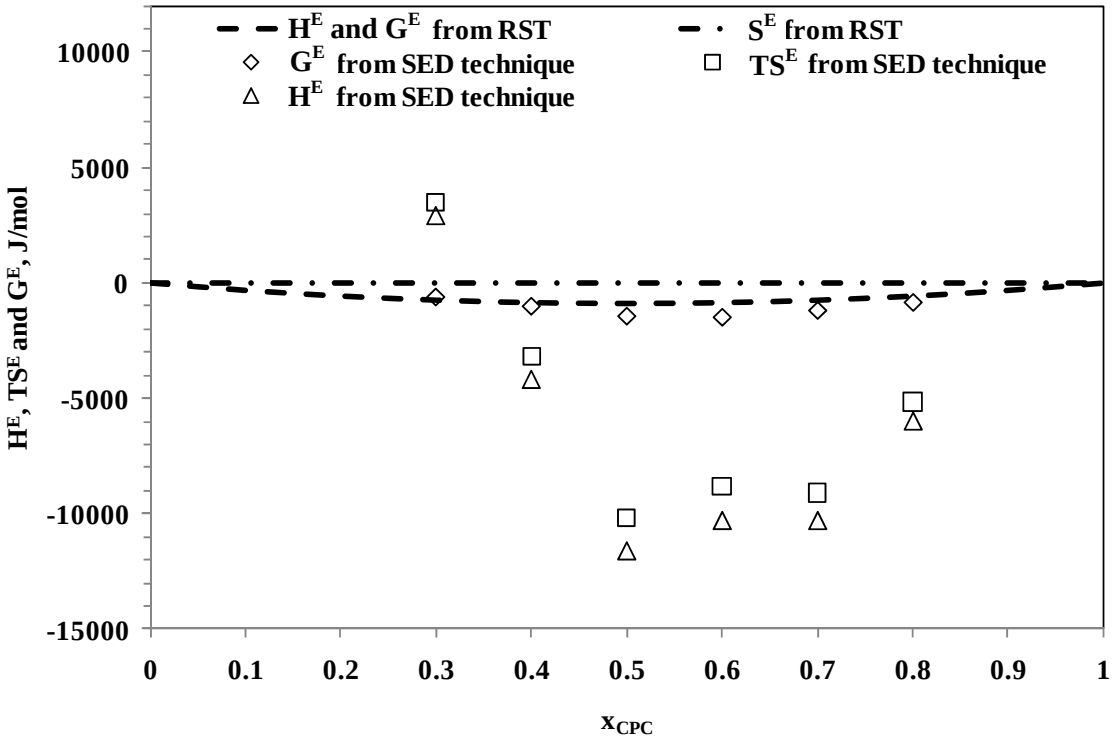

Figure 4.12 Excess enthalpy, excess entropy and excess Gibbs free energy for CPC/NP(EO)$_{10}$ systems at 0.2 M NaCl and 30^{o}C.

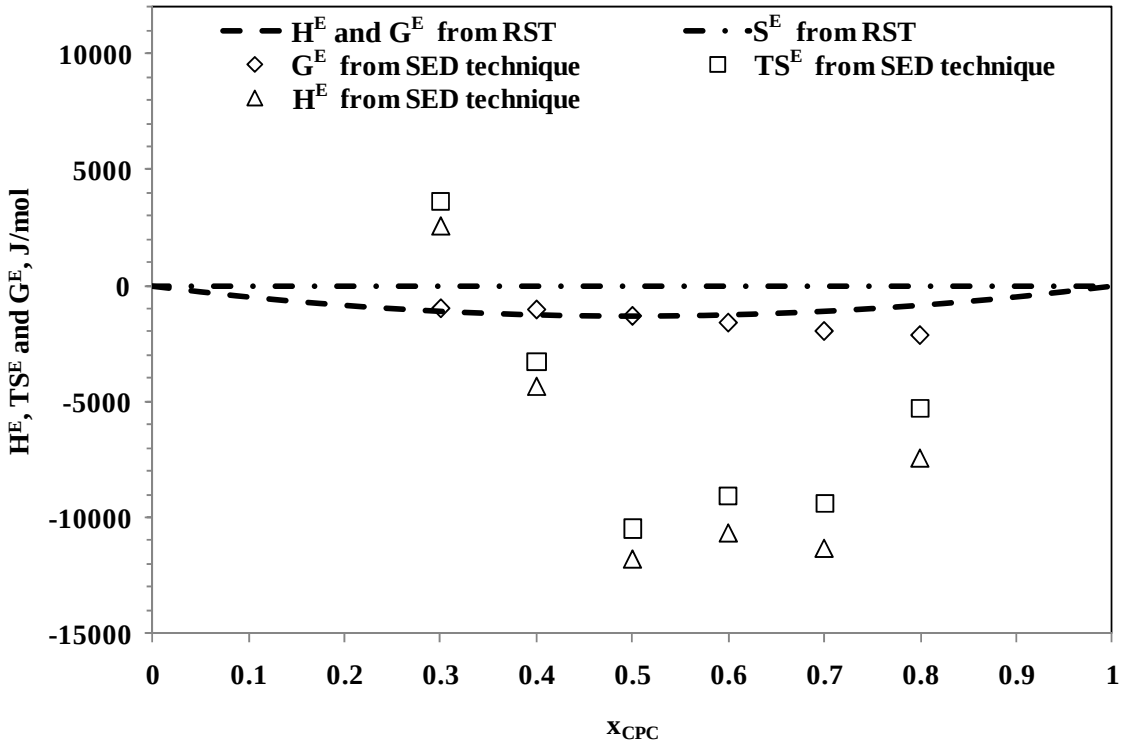

Figure 4.13 Excess enthalpy, excess entropy and excess Gibbs free energy for CPC/NP(EO)$_{10}$ systems at 0.2 M NaCl and 40^{o}C.

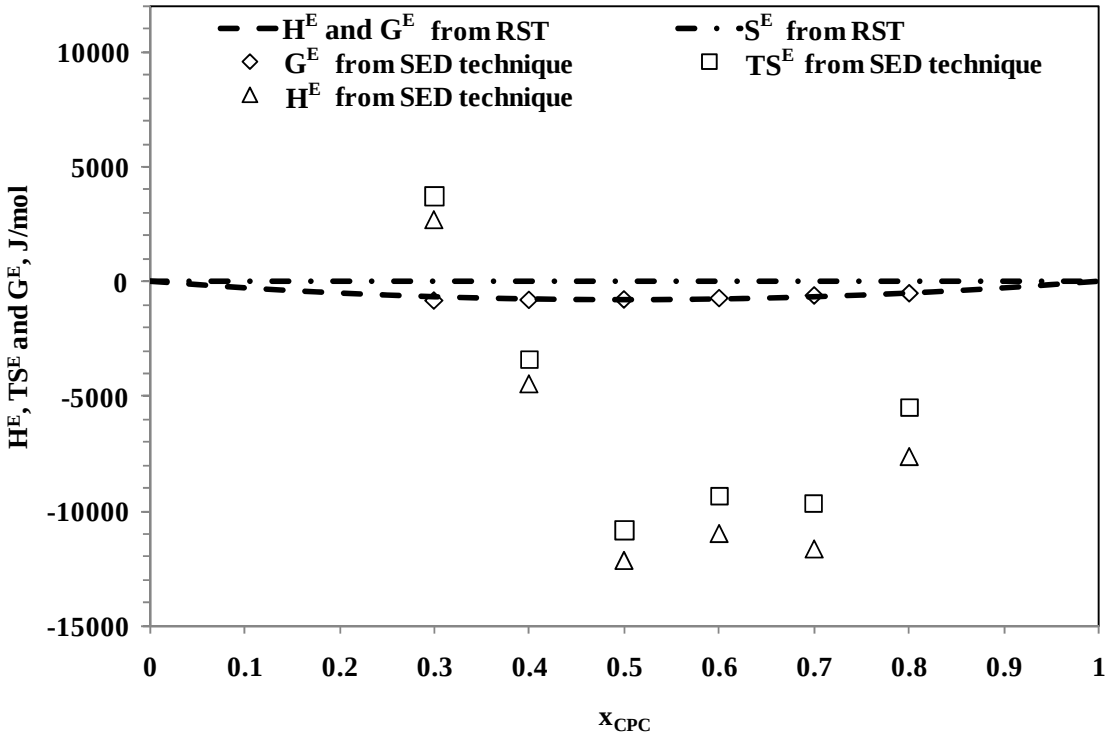

Figure 4.14 Excess enthalpy, excess entropy and excess Gibbs free energy for CPC/NP(EO)$_{10}$ systems at 0.2 M NaCl and 50^{o}C.

4.6 REFERENCES

1. Holland, P. M.; Rubingh, D.N. *J. Phys. Chem.* **1983**, *87*, 1984.

2. Christian, S. D.; Tucker, E. E.; Scamehorn, J. F. In *Mixed Surfactant Systems*, Holland, P.M., Rubingh, D. N., Eds.; ACS Symposium Series 501, American Chemical Society: Washington D.C., 1992; p 45-51.

3. Filipovic-Vincekovic, N.; Juranovic, I.; Grahek, Z. *Colloids Surf., A* **1997**, *125*, 115.

4. Li, F.; Rosen, M. J.; Sulthana, S. B. *Langmuir* **2001**, *17*, 1037.

5. Kharitonova, T. V.; Ivanova, N. I.; Summ, B. D. *Colloid J.* **2002**, *64*, 224.

6. Tsubone, K. *J. Colloid Interface Sci.* **2003**, *261*, 524.

7. Penfold, J.; Staples, E.; Tucker, I.; Thomas, R. K. *Langmuir* **2004**, *20*, 1269.

8. Hierrezuelo, J. M.; Aguiar, J.; Ruiz, C. C. *Colloids Surf., A* **2005**, *264*, 29.

9. Lohateeraparp, P.; Scamehorn, J. F.; Sabatini, D. A. *Langmuir*, submitted.

10. Nishikido, N. *J. Colloid Interface Sci.* **1977**, *60*, 242.

11. Rosen, M. J.; Hua, X. Y. *J. Am. Oil Chem. Soc.* **1982**, *59*, 582.

12. Holland, P. M. In *Structure/Performance Relationship in Surfactants*; Rosen, M. J., Ed.; ACS Symposium Series 253, American Chemical Society: Washington D.C., 1984; p 141-151.

13. Hey, M. J.; MacTaggart, J. W.; Rochester, C. H. *J. Chem. Soc., Faraday I* **1985**, *81*, 207.

14. Holland, P. M. In *Phenomena in Mixed Surfactant Systems*; Scamehorn, J. F., Ed.; ACS Symposium Series 311, American Chemical Society: Washington D. C., 1986; p 102-115.

15. Osborne-Lee, I.; Schechter, R. S.; Wade, W. H.; Barakat, Y. *J. Colloid Interface Sci.* **1985**, *108*, 60.

16. Bansal, V.; Biswas, A.; Balusubramanian, D. *Colloid Polym. Sci.* **1979**, *257*, 1083.

17. Lucassen-Reynders, E. H.; Lucassen, J.; Giles, D. *J Colloid Interface Sci.* **1981**, *81*, 150.

18. de Weerd, R.; de Haan, J.; van de Ven, L.; Buck, H. *J. Phys. Chem.* **1982**, *86*, 2528.

19. Kamrath, R. F.; Franses, E. I. *Ind. Eng. Chem. Fundam.* **1983**, *22*, 230.

20. Haque, M. E.; Das, A. R.; Rakshit, A. K.; Moulik, S. P. *Langmuir* **1996**, *12*, 4084.

21. Hines, J. D.; Thomas, R. K.; Garrett, P. R.; Rennie, G. K.; Penfold, J. *J. Phys. Chem. B* **1997**, *101*, 9215.

22. Lohateeraparp, P.; Scamehorn, J. F.; Sabatini, D. A. *Langmuir*, submitted.

23. Soontravanich, S.; Munoz, J.A.; Scamehorn, J.F.; Harwell, J. H.; Sabatini, D.A. *J. Surfactant Deterg.* **2008**, *11*, 251.

24. Ellott, J.R.; Lira, C.T. *Introductory Chemical Engineering Thermodynamics*; Prentice Hall: New Jersey, 1999; p 359.

25. Ellott, J.R.; Lira, C.T. *Introductory Chemical Engineering Thermodynamics*; Prentice Hall: New Jersey, 1999; p 403.

26. Balzhiser, R. E.; Samuels, M. R.; Eliassen, J. D. *Chemical Engineering Thermodynamics*; Prentice Hall: New Jersey, 1972; p 403-405.

27. Trogus, F. J.; Schechter, R. S.; Wade, W. H. *J. Colloid Interface Sci.* **1979**, *70*, 293.

28. Scamehorn, J. F.; Sabatini, D. A.; Harwell, J. H. In *Encyclopedia of Supramolecular Chemistry*; Atwood, J., Stead, J., Eds; Marcel Dekker: New York, 2004; p 1458-1469.

29. Rathman, J. F.; Scamehorn, J. F. *Langmuir* **1988**, *4*, 174.

30. Rathman, J. F.; Scamehorn, J. F. *Langmuir* **1986**, *2*, 354.

CHAPTER 5

Conclusions and Recommendations for Future Work

5.1 CONCLUSIONS

Overall, the results from this study support the SED technique proposed here for assessing properties of multi-surfactant systems. This technique is convenient and inexpensive when compared to other available techniques. It has a high potential to be a universally applicable method for measuring monomer-micelle equilibrium of multi-surfactant systems.

Although it is time consuming to obtain the kinetic data from SED technique, this method can precisely determine the surfactant monomer and micelle compositions. The values of CMC obtained from this technique show excellent correlation with the data from surface tension measurements and predictions from RST. The SED technique has also shown in this study that although RST describes the CMC data well, the predictions of monomer and micelle compositions from RST can be in gross error. The calculation of excess thermodynamic properties from SED results shows that the excess enthalpies (H^E) and excess entropies (S^E) of mixed micelle formation can be very unsymmetrical with micelle composition for binary ionic/nonionic surfactant micelles. The values of H^E and S^E can be either negative or positive depending on composition.

5.2 RECOMMENDATIONS FOR FUTURE WORK

The use of SED technique to measure monomer-micelle equilibrium may have some limitations needed to be defined in the future. For example, when the initial total concentration of one surfactant in the mixture is less than two times the monomer concentration of this surfactant in the system, the kinetic curve of this surfactant will reach the plateau region before it reaches the real monomer concentration. This will lead to a wrong interpretation of the monomer concentration of this surfactant in the mixture.

This technique also has a potential to extend to investigate some surfactant phenomena (e.g. monomer-micelle-precipitation and monomer-micelle-adsorption equilibriums). A further study is required to determine feasibility and limitation of this extension.