Mixed Micellization of Anionic Ammonium Dodecyl Sulfate and Cationic Octadecyl Trimethyl Ammonium Chloride

Kye-Hong Kang, Hong-Un Kim, Kyung-Hee Lim,* and Noh-Hee Jeong†

Department of Chemical Engineering, Chung-Ang University, Seoul 156-756, Korea
†Department of Industrial and Engineering Chemistry, Chungbuk National University, Cheongju 360-763, Korea

Received February 28, 2001

In aqueous mixtures of cationic OTAC (octadecyl trimethyl ammonium chloride) and anionic ADS (ammonium dodecyl sulfate) surfactants, mixed micelles were formed at low (< 0.2 wt %) total surfactant concentrations. For these mixtures mixed micellization and interaction of surfactant molecules were examined. Mixed critical micelle concentration (CMC), thermodynamic potentials of micellization, and minimum area per surfactant molecule at the interface were obtained from surface tensiometry and electrical conductometry. The mixed micellar compositions and the estimation of interacting forces were determined on the basis of a regular solution model. The CMCs were reduced, although not substantial, and synergistic behavior of the ADS and OTAC in the mixed micelles was observed. The CMC reductions in this anionic/cationic system were comparable to those in nonionic/anionic surfactant systems. The interaction parameter β of the regular solution model was estimated to be –5 and this negative value of β indicated an overall attractive force in the mixed state.

Keywords : Mixed micellization, Vesicle, Ammonium dodecyl sulfate (ADS), Octadecyltrimethyl ammonium chloride (OTAC), Phase behavior.

Introduction

Various surfactants are used widely in diverse applications such as detergents,[1] paints,[2] dyestuffs,[3] cosmetics,[4] pharmaceuticals,[5] pesticides,[6] fibers,[7] foods,[8] plastics,[9] enhanced oil recovery,[10] surface-wetting modification,[11] surfactant-based separation processes,[12] and production of mesoporous catalyst.[13] The surfactants used in a multitude of industrial products, processes, and other practical applications almost always consist of a mixture of surfactants. Therefore, mixed surfactant systems are encountered in nearly all practical applications of surfactants. This is due to the natural polydispersity of commercial surfactants, which result from impurities in starting materials and variability in reaction products during their manufacture.[14] Hence, one has the inherent difficulty preparing chemically and isomerically pure surfactants.

Mixed surfactant systems are much favored from the viewpoint of economy and performance. They are less expensive than isomerically pure surfactants and also they often provide better performance. The latter often arises from the deliberate formulation of mixtures of different surfactant type to exploit synergistic behavior in mixed systems or to provide qualitatively different types of performance in a single formulation. The performance of mixed surfactant systems is often superior to that of a single surfactant system. And practical formulations often require the addition of surfactant additives to help control the physical properties of the product or improve its stability. Hence, it is essential to understanding how surfactants interact in mixtures.[15]

Mixed surfactant systems are also of great theoretical interest. A mixed micellar solution is a representation of a mixed micelle, mixed monolayer at the air/solution interface, and mixed bilayer aggregate at the solid interface. In solutions containing two or more surfactants, the tendency of aggregated structures to form is substantially different from that in solutions having only pure surfactants. Such different tendency results in dramatic change in properties and behavior of mixed surfactants compared to that of a single surfactant.[16] Especially, mixing two surfactant ions of opposite charge, cationic/anionic surfactant mixtures show remarkably different physicochemical properties and behavior. For example, synergistic effects seem to be negligible for mixtures of nonionic surfactants. Ionic/nonionic mixtures, on the other hand, do show appreciable synergism.[17] However, cationic/anionic surfactant mixtures exhibit the largest synergistic effects such as reductions in critical micelle concentration and surface tension.[18] There is a physically simple explanation for enhanced synergism in such mixed charge systems. The basic idea is the hydrophobicity of the salts formed by the strong interactions between two different surfactants with opposite charge.

In this article, we report mixed CMCs, thermodynamic potentials of micellization, and minimum area per surfactant molecule at the air/water interface for aqueous solutions of mixed surfactants of cationic octadecyl trimethyl ammonium chloride (OTAC) and anionic ammonium dodecyl sulfate (ADS). Also we report the mixed micellar compositions and the estimation of interacting forces, which were determined on the basis of the regular solution model.

Cationics are known to exhibit excellent antistatic effects

---

*Corresponding author. Tel: +82-2-820-5275, Fax: +82-2-826-3574; e-mail: khlim@cau.ac.kr

and softness. Hydrocarbons higher than C_{16} are normally employed in cosmetics and toiletries[19,20] and OTAC is probably the most commonly used in these applications. As for anionics, sodium dodecyl sulfate (SDS) is the most well-known, and widely used in industry, and plus it has been extensively studied in relation to its micellization, properties, and phase behavior.[21,22] However, in acidic solutions or at high temperatures, SDS undergoes autocatalytic acid hydrolysis, and dodecanol and sodium hydrogen sulfate are produced.[23-25] These products are believed to cause skin irritation.[25] In contrast, ADS is less hydrolyzed in acidic solutions[26] and less skin-irritative than SDS.[27,28] For these reasons, the use of ADS and OTAC in the cosmetic and toiletry industry has been expanding.[29,30] However, little has been conducted on the micellization of these surfactants, and the CMC has only been reported at two or three different temperatures.[31] Accordingly, this is the reason why ADS and OTAC were selected as the surfactants in the current study.

In the mixed surfactant systems studied in this article, surface tension reductions and synergistic behavior of ADS and OTAC were observed. The interaction parameter β of the regular solution model was estimated to be -5 and this negative value of β indicated an overall attractive force in the mixed state. This small negative value was comparable to that of a nonionic/anionic mixed surfactant system.[32]

Experimental Section

Materials. The cationic surfactant octadecyltrimethyl ammonium chloride (OTAC) and anionic surfactant ammonium dodecyl sulfate (ADS) were purchased from Fluka. OTAC had a stated purity of 98% and ADS was in a form of 30% aqueous solution. For further purification the surfactants were first placed in a rotary evaporator to reduce the water and volatile material content. Then, OTAC was recrystallized twice from absolute ethanol. ADS was also recrystallized first from 90% ethanol and then twice from absolute ethanol. The purified surfactants were finally dried in an evacuated desiccator.[33] Water was distilled and deionized.

Electrical Conductivity Measurements. The critical micelle concentrations (CMC's) were determined by electrical conductometry and interfacial tensiometry. For conductivity measurements of the surfactant solutions, a Radiometer (Paris, France) Model CDM 210 conductivity meter and a Model CDC641T conductivity cell with platinized electrodes were used. Platinized platinum electrodes were chosen to improve the accuracy of the conductivities by reducing any electrode polarization effects. The conductivity cell was calibrated with standard solutions and its cell constant was determined to be 0.7443 cm^{-1}. The surfactant concentrations were changed by additions of deionized water from a burette to the surfactant solution, which was contained in a jacked, thermostatted beaker. The surfactant solution was mixed thoroughly by magnetically driven stirring. The temperature was controlled within 0.1 ^{o}C by a thermostat bath (Model VS-1205WP-CWO, Vision Scientific, Seoul, Korea).

Surface Tension Measurements. The surface tensions of surfactant solutions were measured with a du Noüy KSV (Helsinki, Finland) Model Sigma 70 tensiometer using a platinum ring. The surfactant solutions were added by a microsyringe to water in a thermostatted glass vessel, and the surface tension was measured after thorough mixing with a magnetic stirrer. The temperature of the surfactant solutions was controlled within 0.1 ^{o}C by a Jeio Tech (Seoul, Korea) Model VTRC-620 thermostat bath.

Zeta-Potential Measurements. The ζ potentials of the mixed micelles were measured by ZetaSizer 2000 (Malvern Instruments Ltd.). The principle on which the measurements were based was the Doppler electrophoresis with light scattering. The samples of ADS/OTAC mixtures with the ADS mole fraction of 0, 0.1, 0.3, 0.5, 0.7, 0.9, and 1 were prepared at the total surfactant concentrations slightly above the CMCs, so that there were particles enough not to cause multiple scattering. Also, the samples without dilution were used for the measurements. Each sample was injected to the cell by the syringe and at this time care had to taken of not producing bubbles in the cell. If the bubbles were produced in the cell, their movement would be seen as the movement of particles and would change the result. The viscosity of 1.002 cP and dielectric constant of 80.4 were used for the calculations, since the solvent used was DI. water and the very small amount of surfactants used would make presumably these values changed little.

Results and Discussion

Mixed Micellization. The phase diagram of very dilute aqueous mixtures of anionic ADS and cationic OTAC is presented in Figure 1 in a rectangular coordinate. The concentration of each surfactant was less than 0.2 wt %. The phase diagram is characterized by four distinct phase regions. Those are the regions of isotropic molecular solution (I), micellar solution (M), vesicles (V), and mixture of micelles and vesicles (M+V). Further details on the phase diagram may be found elsewhere.[34]

The isotropic solution is clear and its region (I) is extended up to the pure component CMCs in aqueous solutions that are 0.392 m molal (0.0137 wt fraction) for OTAC and 6.258 m molal (0.1771 wt fraction) for ADS, respectively.[35] The isotropic solution region on the ADS-rich side is wider than that on the OTAC-rich side because of the disparity in CMC (CMC of ADS is about 20 times larger than that of OTAC). The OTAC-rich isotropic region is seen very small near the water apex in a triangular coordinate.

In the micellar region (M) mixed micelles of ADS and OTAC were formed. The mixed CMC remained unchanged with the mole fraction of ADS, α up to 0.7, and then increased rapidly. As α increased from 0.1 to 0.5, the micellar region shrank and for $0.5 < \alpha < 0.7$ it was too narrow to be observed. Hence, for these α values, the isotropic fluid region is apparently on direct contact with the vesicular region.

In the region denoted as V, the mixture fluid was turbid and the turbidity appeared to increase with total surfactant

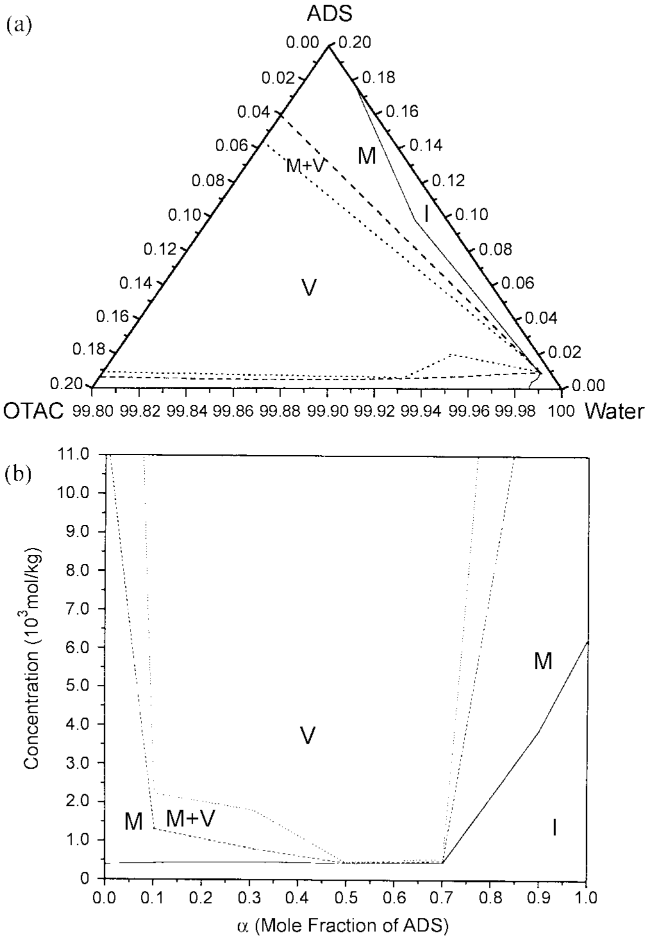

Figure 1. Phase behavior of OTAC/ADS/Water systems with high water content at 30 °C, in triangular coordinates (a) and rectangular coordinates (b).

concentration. At the fixed total surfactant concentration the turbidity increased with α. In this region the existence of vesicles was confirmed by negative staining transmission electron microscopy (TEM). A couple of TEM micrographs of vesicles are shown in Figure 2 and details on the vesicles will be presented in a separate article.[34]

Over the phase regions of the isotropic (I) and the micellar (M), the critical micelle concentrations of the pure and the mixed surfactant systems were determined by measuring surface tensions and electrical conductivities. The surface tension results are presented in Figure 3 and summarized in Table 1. For the surface tension *vs*. concentration data, the CMC was taken as the concentration where the surface tension changed its trend. As the total surfactant concentration increased, the surface tension decreased below CMC and remained almost constant above CMC.

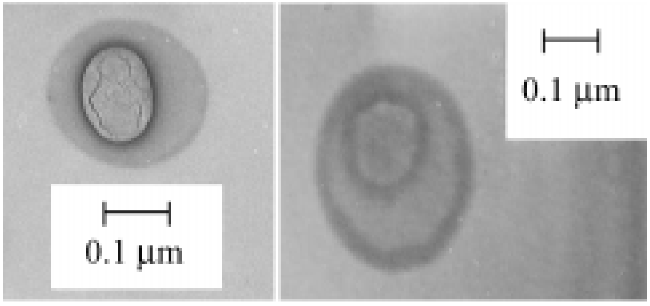

Figure 2. Transmission electron microscopy (TEM) micrographs of vesicles of ADS/OTAC mixed surfactant systems at the mole fraction of ADS of 0.7018.

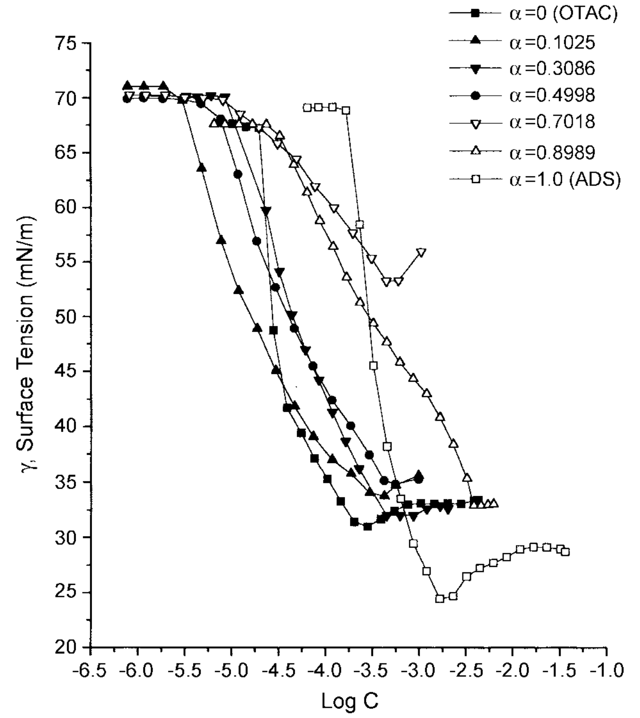

Figure 3. Surface tension *vs*. logarithm of total surfactant concentration at 30 °C for OTAC/ADS mixed systems at different mole fractions α of ADS.

From the electrical conductivity data the CMC was determined as the point where the two lines met each other. Figure 4a shows the conductivity results for the aqueous mixed surfactant solutions with α=0.1025. The conductivity exhibited distinct linear behavior before and after the CMC and therefore the intersect of the lines was taken as the CMC. The CMCs by these two methods are in good agreement with each other at small α values; they differ by 5%. This 5% difference is not surprising, because the CMC is, in

Table 1. Mixed CMC's at 30 °C at relative mole fractions α of ADS to OTAC

	Mixed CMCs (mol/kg)	
	Surface Tension	Electrical Conductivity
0.0	0.392	0.348
0.1025	0.428	0.451
0.3086	0.452	–
0.4998	0.426	–
0.7018	0.453	–
0.8989	3.861	–
1.0	2.512	6.646

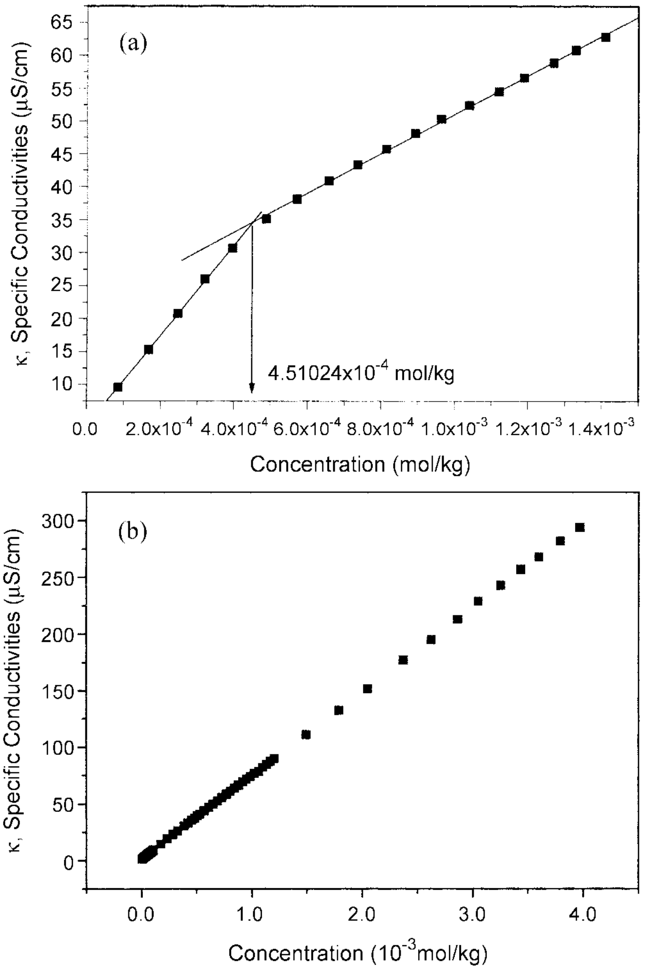

Figure 4. Specific conductivity *vs*. total surfactant concentration at 30 °C for an OTAC/ADS mixed system; a ($\alpha = 0.7018$) and b ($\alpha = 0.1025$).

fact, a range, though narrow, of concentration and because various experimental methods tend to probe slightly different CMCs. At α=1.0 the CMC of ADS determined by tensiometry was substantially smaller than that by electrical conductometry. The latter value agreed with the value of 6.6 mM reported in the literature.[31] At four intermediate values of α on Table 1, the CMC could not be determined from the conductivity data. For these values of α the conductivity appeared to have no change in slopes, as shown in Figure 4b. In contrast to the mixed surfactant systems, those of pure ADS and OTAC exhibited sharp changes in slopes for the electrical conductivity data.[35]

Molecular Interactions and Synergistic Effect. The CMCs, C_{12}^M, of the mixed ADS/OTAC system varied with the relative amount of the surfactants. Figure 5 shows C_{12}^M as a function of mole fraction, α, of ADS in the total surfactant. At small α values C_{12}^M was almost identical to the CMC, C_1^M, of pure OTAC and remained almost unchanged up to α=0.7. Then C_{12}^M increased rapidly to the CMC, C_1^M, of pure ADS.

The regular solution model was applied to find the mole fraction X_1 of ADS in the micelle and the interaction parameter β using the values of C_1^M, C_2^M, C_{12}^M, and equations (1) and (2).[36, 37]

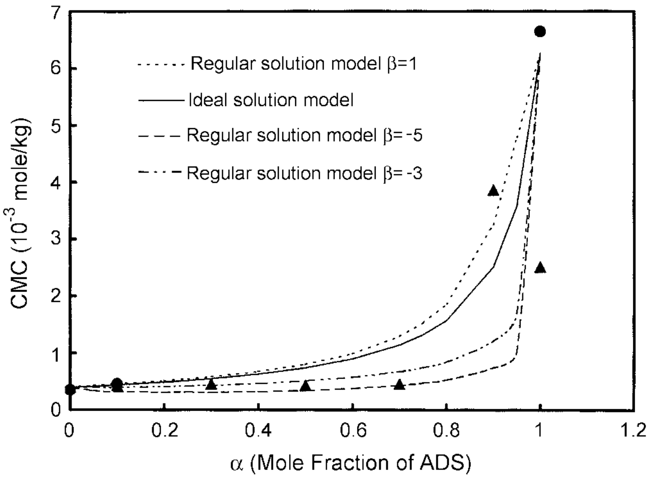

Figure 5. Mixed CMCs (Δ by tensiometry and • by electrical conductometry) of OTAC/ADS mixed systems compared to the theoretically predicted CMCs for various β values.

$$\frac{(X_1)^2\ln\left(\frac{C_{12}^M\alpha}{C_1^M X_1}\right)}{(1-X_1)^2\ln\left(\frac{C_{12}^M(1-\alpha)}{C_2^M(1-X_1)}\right)} = 1 \qquad (1)$$

$$\beta = \frac{\ln[\alpha C_{12}^M/(X_1C_1^M)]}{(1-X_1)^2} = \frac{\ln[(1-\alpha)C_{12}^M/((1-X_1)C_1^M)]}{X_1^2} \qquad (2)$$

With X_1 these and β values, C_{12}^M of the ADS/OTAC were calculated by equation (3) and (4a) or (4b).[38]

$$\frac{X_1(1-\alpha)C_1^M\exp(\beta(1-X_1)^2)}{(1-X_1)\alpha C_2^M\exp(\beta(X_1)^2)} = 1 \qquad (3)$$

$$\alpha C_{12}^M = X_1C_1^M\exp[\beta(1-X_1)^2] \qquad (4a)$$

$$(1-\alpha)C_{12}^M = (1-X_1)C_2^M\exp[\beta(X_1)^2] \qquad (4b)$$

The curves in Figure 5 represent the C_{12}^M calculated by these equations for different β values. The measured C_{12}^M deviated negatively from the ideal solution model (β=0), and followed most closely by the model with β=–5. This negative value of β indicates synergistic behavior of the components of ADS and OTAC in the mixed micelle, and is quite comparable to β=–4.3 for the mixed CMCs of sodium deoxycholate and Tween 80.[32] At α=0.8989 the mixed CMC was much higher than the others at smaller α's, and it has been reported that mixtures of surfactants can feign a wrong CMC value, when the component with the much higher CMC has the highest mole fraction.[39]

The mole fraction X_1 of ADS in the mixed micelles increased with α, as expected (Table 2). At all α's the mole fraction of OTAC was larger, implying that OTAC was the majority in the mixed micelles. At α=0.8989, X_1 was

Table 2. Mixed CMC's at 30 °C at relative mole fractions α of ADS to OTAC

α	X_1	H^E/RT	f_{ADS}	f_{OTAC}	(Å^2)
0.0					61
0.1025	0.0200	−0.0213	0.3514	0.9996	56
0.3086	0.1524	−0.3455	0.1463	0.9398	55
0.4998	0.2727	−0.7802	0.1248	0.7464	55
0.7018	0.3601	−1.1029	0.1409	0.5375	63
0.8989	0.0054	0.0250	103.4	1.0001	58
1.0					47

calculated to be 0.0054. It is surprising that the mixed micelles are made up mainly of OTAC at this high α value, *i.e.*, at this high overall concentration of ADS.

The excess enthalpy H^E of the micellization is ordinarily described by the regular solution model as the equation[40]

$$H^E = X_1(1-X_1)\beta RT = G^E \tag{5}$$

where βRT represents the difference in interaction energy between the mixed and unmixed systems. Equation 5 corresponds to the leading term in the lattice model description for the enthalpy of mixing in liquid mixtures.[41] H^E of the mixed micellization was calculated by this equation and the results are presented in Table 2. H^E was negative except at $\alpha = 0.8989$. These negative values signify that the mixed micellization of OTAC and ADS is exothermic. Since it is assumed that the excess entropy is zero in the regular solution model, the excess Gibbs free energy G^E is indistinguishable from H^E, and also is given by eq. 5.

The activity coefficients f_{ADS} and f_{OTAC} are related to G^E by the equation[40]

$$G^E/RT = X_1 \ln f_{ADS} + (1-X_1) \ln f_{OTAC} \tag{6}$$

Substitution of eq. 5 for G^E to eq. 6 yields the following expressions for f_{ADS} and f_{OTAC}:

$$f_{ADS} = \exp[\beta(1-X_1)^2] \tag{7}$$

$$f_{OTAX} = \exp[\beta X_1^2] \tag{8}$$

With these equations f_{ADS} and f_{OTAC} were calculated and the results are tabulated in Table 2. The activity coefficients were less than 1 (except at $\alpha = 0.8989$), and f_{ADS} was smaller than f_{OTAC}. Since f_{OTAC} was closer to 1 than f_{ADS}, ADS appeared to be more responsible for nonideality in the ADS/OTAC mixtures.

Interfacial Adsorption and Area per Surfactant Molecule. Surfactant molecules are usually adsorbed at the air-water interface and this adsorption results in the surface tension reduction. The concentration-dependent adsorption at the interface is described by the Gibbs adsorption equation. For aqueous solutions of mixed surfactants the Gibbs surface excess Γ_i of component i is related to the surface tension γ by the equation

$$-d\gamma = \sum_i \Gamma_i RT \ln C_i \tag{9}$$

where C_i is the concentration of the i-th component, R is the gas constant, and T is the Kelvin temperature. The component and total mass balances may yield the following equation:

$$\Gamma_{\max} = -\frac{1}{2RT} \lim_{c \to cmc} \frac{d\gamma}{d\ln C_{tot}}. \tag{10}$$

Here, C_{tot} is the total surfactant concentration and $\Gamma_{\max}$ is the maximum surface excess. Using $\Gamma_{\max}$ the minimum area $a_{\min}$ per surfactant molecule was calculated by $a_{\min} = (N_{av}\Gamma_{\max})^{-1}$ with N_{av} being the Avogadro's number, and summarized in Table 2. For pure components ADS and OTAC, the hydrophilic head area $a_{\min}$ for OTAC was larger than that for ADS, as expected. In the mixed system $a_{\min}$ was smaller than $a_{\min}$ for OTAC alone. This finding is in agreement with early studies which revealed that in the mixed cationic-anionic surfactant systems, the mean head size in an organized assembly would become rather small.[42,43] This is due to the strong molecular interaction between the two oppositely charged surfactant ions, which is omni-present in many mixed catanionic surfactant systems.[44,45] As the fraction of ADS increased in the mixed system, $a_{\min}$ increased slightly from 55 to 58 Å^2. At $\alpha = 0.7018$, $a_{\min}$ became substantially larger. This larger value of $a_{\min}$ may be due to vesicles coexisting with micelles, because at this α value the micellar region is very narrow and neighbors with the vesicle region, as seen in Figure 1b.

Zeta Potentials of Mixed Micelles. Zeta potentials of the mixed micelles were measured and the results are presented in Fig. 6. The zeta potentials were large in magnitude. For pure OTAC and ADS micelles the zeta potentials were +98.2 mV and −115.7 mV, respectively and ζ potentials of the mixed micelles at different α's fell between those of the pure-component micelles. As α increased, ζ potential decreased and became negative beyond $\alpha = 0.7$. It is interesting to observe that the zeta potentials at $\alpha = 0.7$ and 0.9 is negative, although OTAC is still the major surfactant in the mixed micelles at these high ADS concentrations. There is virtually no micellar region between $\alpha = 0.5$ and 0.7, as shown in Fig. 1b. Hence, zeta potentials of the mixed micelles could not be measured between these α values. The ζ potentials at $\alpha = 0.5$ and 0.7 in Fig. 6 were those of the

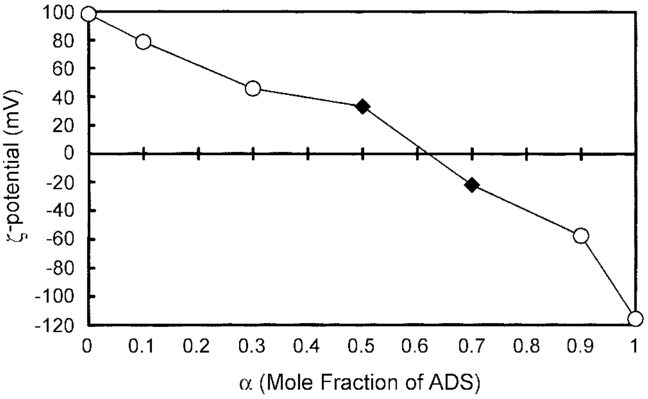

Figure 6. Zeta potentials of the mixed ADS/OTAC micelles at different mole fractions of ADS, α. At $\alpha = 0.5$ and 0.7 the zeta potentials were those of the vesicles.

vesicles, because they were measured in the vesicular region slightly above the phase boundary.

Conclusions

The mixed CMCs of anionic surfactant ADS and cationic surfactant OTAC at their different compositions were measured using surface tensiometry and electrical conductometry. Although it was not substantial, surface tension reduction was observed and therefore ADS and OTAC exhibited synergistic behavior in the mixed micelles. The synergistic effect was comparable to that of nonionic/anionic mixed systems.

The interaction parameter β was estimated to be -5 on the basis of the regular solution model and the excess enthalpy of micellization was negative, implying that the mixed micellization was exothermic. The minimum area $\alpha_{\min}$ of the mixed surfactants at the air/water interface lie between the values of pure components, which was in good qualitative agreement with previous studies.

References

1. Cutler, W. G.; Kissa, E. *Detergency: Theory and Practice*; Marcel Dekker: New York, 1987.
2. Stoye, D. *Paints, Coatings and Solvents*; VCH: Weinheim, 1993.
3. Luck, P. *J. Soc. Dyers Colourists* **1958**, 74.
4. Reiger, M. M. *Surfactants in Cosmetics*; Marcel Dekker: New York, 1985.
5. Elworthy, P. H.; Florence, A. T.; Macfarlane, C. B. *Solubilisation by Surface Active Agent*; Chapman and Hall: London, 1968.
6. Becher, P. *Encyclopedia of Emulsion Technology*; Marcel Dekker: New York, 1985; Vol. 2.
7. Jacobi, G.; Löhr, A. *Detergents and Textile Washing*; VCH: Weinheim, 1987.
8. Friberg, S. E. *Food Emulsions*; Marcel Dekker: New York, 1976; Vol. 5.
9. Milton, M. J. *Surfactants in Emerging Technology*; Marcel Dekker: New York, 1987.
10. Shah, D. O.; Schechter, R. S. *Improved Oil Recovery by Surfactant and Polymer Flooding*; Academic Press: New York, 1977.
11. Rimai, D. S.; DeMejo, L. P.; Mittal, K. L. *Fundamentals of Adhesion and Interfaces*; VSP: Utrecht, 1995.
12. Scamehorn, J. F.; Harwell, J. H. *Surfactant-Based Separation Processes*; Marcel Dekker: New York, Surfactant Science Series, Vol. 33, 1989.
13. Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.
14. Scamehorn, J. F. *Phenomena in Mixed Surfactant Systems*; Am. Chem. Soc.: Washington, DC, 1986.
15. Holland, P. M.; Roubingh, D. N. *Mixed Surfactant Systems*; Am. Chem. Soc.: Washington, DC, 1992.
16. Ogino, K.; Abe, M. *Mixed Surfactant Systems*; Marcel Dekker: New York, 1993.
17. Rosen, M. J.; Hua, X. Y. *J. Am. Oil Chem. Soc*. **1982**, *59*, 582.
18. Lucassen-Reynders, E. H.; Lucassen, J.; Giles, D. *J. Colloid Interf. Sci*. **1981**, *81*, 150.
19. Allardice, A.; Gummo, G. *Cosmet. Toilet.* **1988**, *108*, 107.
20. Jurczyk, M. F.; Berger, D. R.; Damaso, G. R. *Cosmet. Toilet.* **1991**, *106*, 63.
21. Kekicheff, P.; Grabielle-Madelmont, C.; Ollivon, M. *J. Colloid Interf. Sci*. **1989**, *131*, 112.
22. Kekicheff, P. *J. Colloid Interf. Sci*. **1989**, *131*, 133.
23. Kurz, J. L. *J. Phys. Chem*. **1962**, *66*, 2239.
24. Muramatsu, C.; Inoue, M. *J. Colloid Interf. Sci*. **1976**, *55*, 80.
25. Rosen, M. J. *Surfactants and Interfacial Phenomena*, 2nd ed.; Wiley: New York, 1989; p 14.
26. Porter, M. R. *Handbook of Surfactants*; Chapman and Hall: New York, 1991; p 70.
27. Rosen, M. J. *Surfactants and Interfacial Phenomena*, 2nd ed.; Wiley: New York, 1989; p 15.
28. Porter, M. R. *Handbook of Surfactants*; Chapman and Hall: New York, 1991; p 73.
29. Fox, C. *Cosmet. Toilet.* **1988**, *103*, 25.
30. Hunting, A. L. *Encyclopedia of Shampoo Ingredients*; Micelle Press: London, 1983.
31. Mukerjee, P.; Mysel, K. J. *Critical Micelle Concentrations of Aqueous Surfactant Systems*; NSRDS-NBS 36; National Bureau of Standards: Washington, D. C., 1971.
32. Haque, M. E.; Das, A. R.; Moulik, S. P. *J. Colloid Interf. Sci.* **1999**, *217*, 1.
33. Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*; Butterworth Heinemann: Oxford, 1996.
34. Kang, K.-H.; Kim, H.-U.; Lim, K.-H. manuscript in preparation.
35. Kang, K.-H.; Kim, H.-U.; Lim, K.-H. *Colloids Surf. A* **2001**, *189*, 113.
36. Holland, P. M.; Roubingh, D. N. *J. Phys. Chem*. **1983**, *87*, 1984.
37. Mittal, K. L. *Solution Chemistry of Surfactants*; Plenum Press: New York, 1979.
38. Hua, X. Y.; Rosen, M. J. *J. Colloid Interf. Sci*. **1982**, *90*, 212.
39. Yu, Z. J.; Zhao, G. X. *J. Colloid Interf. Sci*. **1989**, *130*, 414.
40. Holland, P. M. *Adv. Colloid Interf. Sci.* **1986**, *111*, 26.
41. Münster, A. *Statistical Thermodynamics*; Springer: New York, **1974**; Vol. 2, p 650.
42. Hua, X. Y.; Zhao, G. X. *Acta Chim. Sinica* **1965**, *3*, 441.
43. Zhao, G. X.; Ou, J. G.; Tian, B. S.; Huang, Z. M. *Acta Chim. Sinica* **1980**, *38*, 409.
44. Yu, Z. J.; Zhao, G. X. *J. Colloid Interf. Sci.* **1989**, *130*, 432.
45. Li, X. G.; Zhao, G. X. *Colloids Surf.* **1992**, *64*, 185.