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Micellar Shape Driven Counterion Binding. Small-Angle Neutron Scattering Study of AOT Micelle

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Sodium dioctylsulfosuccinate (AOT) micelle has a special counterion binding behavior in aqueous electrolyte medium, viz., the counterion binding constant (β) abruptly increases by 2-fold at about 0.015 mol dm^{-3} NaCl concentration (c^*), but not in sodium salicylate (NaSa) solution. Since counterions affect the structure and performance of ionic surfactants, ascertaining the cause for the sudden shift in the β value of AOT micelle is of fundamental importance. In this study the special counterion binding behavior of AOT micelle has been ascertained at 40 °C by carrying out surface tension, zeta potential, and fluorescence emission (pyrene probe) measurements. The results of the small-angle neutron scattering experiment carried out at 40 °C showed that at c^* the shape of AOT micelle changes from prolate spheroid to rodlike in NaCl solution, but not in NaSa solution, thus establishing micellar shape change as responsible for the abrupt change in β value. The absence of sudden shift in β of AOT micelle in NaSa solution is attributed to the binding of salicylate coanion to AOT micelle through hydrophobic interaction.

Introduction

Sodium dioctylsulfosuccinate (AOT), a double-chained anionic surfactant, has an unique type of counterion binding behavior in the presence of electrolytes.[1,2] In aqueous NaCl solution, the counterion binding constant (β) for AOT is about 0.4 when NaCl concentration is less than 0.015 M (M = mol dm^{-3}), and a sudden 2-fold increase in the value of β occurs when NaCl concentration becomes about 0.015 M (c^*). The occurrence of such a sudden shift in the value of β of AOT micelles at c^* has been confirmed in the presence of different sodium salts,[1,2] but surprisingly not in aqueous sodium salicylate (NaSa) medium.[3]

A change in the value of β in the presence of added electrolyte has been reported in the case of a few more ionic surfactants,[4−10] but in all these cases the change occurred at fairly high electrolyte concentration (≥ 0.1M) and it was attributed to the salting-out effect. AOT is the only example known presently where change in β occurs at a very low electrolyte concentration. In light of the reported[11−14] phase behavior studies of the AOT−water system in the absence and presence of NaCl, it is clear that the sudden change in β cannot be due to a phase change.

Counterion binding ability is one of the important characteristics of ionic micelles since counterions are known to influence cmc values of ionic surfactants, size and shape of ionic micelles, and also reactions in solutions of ionic surfactants. Therefore, it is of fundamental importance to ascertain the cause for the sudden shift in the β value of AOT micelle. It has been proposed that a change in micellar shape may be responsible for the shift in the counterion binding.[1,15] However, no experimental evidence is available to confirm this proposition in AOT + water + salt system. With this objective in mind, we carried out small-angle neutron scattering (SANS) measurements of AOT + D$_2$O + NaCl/NaSa systems, and the results are presented in this paper.

Experimental Section

AOT (Sigma, 99% assay), NaCl (Merck, 99.5% assay), and NaSa (Fluka, ≥99.5% assay) were used without further purification. Stock solutions of AOT and the salts were prepared in Milli-Q water, and the required concentrations were obtained by dilution in the case of all measurements other than SANS and NMR measurements. Solutions for SANS measurements were prepared in D$_2$O (99.4 atom % D), which was obtained from the Heavy Water Division, BARC, Trombay. During SANS measurements on AOT, low solubility of AOT in D$_2$O (as well as water) posed a problem because of low SANS intensity. Hollamby et al.[16] had also pointed out about this particular problem with SANS study of AOT. The solubility of AOT in water and D$_2$O decreased further in the presence of NaCl. We therefore had to fix the AOT concentration at 15 mM (~0.7 wt %) and carry out SANS measurements at 40 °C. This necessitated verification of the abrupt change in β value of AOT at 40 °C, since all earlier measurements were at 25 °C. Therefore, in addition to SANS, we also carried out surface tension measurement of AOT in aqueous NaCl and NaSa solutions at 40 °C to determine cmc as a function of electrolyte concentration. Surface tension measurements were

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made by the Wilhelmy plate method using a Krüss K11 tensiometer attached with a thermostat (Haake DC 10).

SANS experiments were carried out at the Dhruva Reactor, Bhabha Atomic Research Center, Trombay, India. The SANS diffractometer makes use of a beryllium oxide filtered neutron beam of mean wavelength (λ) 5.2 Å, and the data were collected within the Q (scattering vector $Q = 4\pi \sin \theta/\lambda$, where 2θ is the scattering angle) range of 0.02−0.20 Å^{-1}. The samples were taken in quartz sample holder of 0.5 cm path length having tight fitting Teflon stopper. The concentration of AOT was fixed at 15 mM, and the concentrations of NaCl and NaSa were varied from 5 to 15 mM. The measured SANS distributions were corrected for the background, empty cell scattering, and the sample transmission, and the corrected data were then normalized to absolute cross sectional unit using standard procedures.[17]

The analysis of the SANS data was done according to the procedure described elsewhere[18,19] by one of the coauthors. In this method of data analysis, the differential scattering cross section per unit volume ($d\Sigma/d\Omega$) is represented by the expression

$$d\Sigma/d\Omega = n(\rho_m - \rho_s)^2 V^2 [\langle F^2(Q)\rangle + \langle F(Q)\rangle^2(S(Q)-1)] + B \quad (1)$$

In eq 1, ρ_m and ρ_s denote the scattering length densities of the micelle and the solvent, respectively, n is the number density of the micelles, V is the volume of the micelle, $F(Q)$ is the single particle form factor, $S(Q)$ is the interparticle structure factor, and B is a constant term. $F(Q)$ depends on the shape and size of the particles, and $S(Q)$ is decided by the spatial distribution of the particles. B accounts for the incoherent scattering background that occurs in the case of neutrons mainly due to the presence of hydrogen in the sample. The relations used for prolate ellipsoidal micelles are

$$\langle F^2(Q)\rangle = \int_0^1 F(Q,\mu)^2 \, d\mu \quad (2)$$

$$\langle F(Q)\rangle^2 = [\int_0^1 F(Q,\mu) \, d\mu]^2 \quad (3)$$

$$E(Q,\mu) = 3(\sin x - x \cos x)/x^3 \quad (4)$$

$$x = Q[a^2\mu^2 + b^2(1-\mu^2)]^{1/2} \quad (5)$$

In eq 5, a and b are the semimajor and semiminor axes of the ellipsoidal micelle, respectively. The term μ in the above equations refers to the cosine of the angle between the directions of a and Q. In the analysis of SANS data the ellipsoidal shape ($a \neq b = c$) of the micelles is widely used because it can represent other different probable shapes like spherical ($a = b$) and rodlike ($a \gg b$). The expression for $S(Q)$ is given by the Fourier transform of the radial distribution function $g(r)$. $g(r)$ gives the probability of finding the center of another micelle at a distance r from the center of a reference micelle. $S(Q)$ is calculated using the mean spherical approximation developed by Hayter and Penfold.[20] In this approximation, the micelle is treated as a rigid equivalent sphere of diameter $d = 2(ab^2)^{1/3}$ interacting with another micelle through a screened coulomb potential $u(r)$ given by the relation

$$u(r) = u_0 d \exp[-\kappa(r-d)]/r, \quad r > d \quad (6)$$

where u_0 is the potential at $r = d$ and the Debye−Hückel inverse screening length κ is evaluated by using the expression

$$\kappa = \left(\frac{8\pi N_A e^2 I}{10^3 \varepsilon k_B T}\right)^{1/2} \quad (7)$$

In eq 7, N_A, e, ε, k_B, and T denote Avogadro number, electronic charge, dielectric constant of the solvent, Boltzmann constant, and absolute temperature, respectively. The ionic strength I of the micellar solution is calculated as

$$I = \text{cmc} + 0.5\alpha c + c_e \quad (8)$$

where c and c_e are the concentrations of the surfactant and electrolyte in the solution, respectively. α is the fractional charge, which is equal to the micellar charge (Z) divided by the aggregation number (N). The contact potential u_0 is calculated as

$$u_0 = \frac{z^2 e^2}{\pi \varepsilon \varepsilon_0 d(2+\kappa d)^2} \quad (9)$$

where ε_0 is the permittivity of vacuum. To simplify calculations, polydispersity of micelles was ignored and the micellar solution was considered to have monodisperse ellipsoids only.

We also made at 40 °C zeta potential (using Malvern Zetasizer 3000HS instrument) and fluorescence emission (using Hitachi F4500 FL spectrophotometer; pyrene probe) measurements in AOT + NaCl + H$_2$O and AOT + NaSa + H$_2$O systems. ^{1}H NMR spectra of solutions of NaSa in D$_2$O (Aldrich, 99.9 atom % D) in the absence and presence of AOT were recorded at 25 °C on a Bruker Avance II-400 spectrometer operating at 400 MHz with TMS as the internal reference.

Results and Discussion

Critical Micelle Concentration and Counterion Binding. Critical micelle concentration (cmc) values of AOT at 40 °C in aqueous NaCl and NaSa solutions determined from the measured surface tension data are (Figure 1a) found to be less than those reported[1] at 25 °C, which is attributed to endothermic micellization of AOT in water.[21]

The values of β of AOT micelle in aqueous NaCl and NaSa media at 40 °C were calculated using the Corrin−Harkins (CH) equation, ln cmc $= A - \beta \ln C_c$, where C_c is the concentration of counterion in the solution and A is a constant related to the standard free energy of micellization. From the CH plot (Figure 1b) it is clear that in aqueous NaCl solution the special counterion binding behavior of AOT reported[1] earlier at 25 °C prevails at 40 °C also. The values of β at 40 °C are found to be 0.45 below c^* and 0.85 above c^*. Similarly, in the presence of NaSa at 40 °C, as observed previously[3] at 25 °C, β has only one value equal to 0.45. Thus, the counterion binding behavior of AOT is same at 25 and 40 °C.

SANS. The values of $d\Sigma/d\Omega$ as a function of scattering vector Q obtained from SANS experiments at 40 °C are shown in Figure 2. For AOT, the values of the semiminor axis and the volume (v) of the monomer with headgroup were taken from the literature[22] as 12.6 and 611 Å^3, respectively. The values of the aggregation number ($N = 4\pi ab^2/(3v)$), fractional charge, and the axial ratio a/b determined from the fitting are shown in Figure 3. The SANS spectrum of AOT in D$_2$O with no salt shows the characteristic correlation peak at $Q \approx 0.059$ Å^{-1}, which is in good agreement with the literature[22] value, and this peak is indicative of repulsive interactions operating between the negatively charged AOT micelles. From the present data analysis, we obtained for AOT in D$_2$O aggregation number = 30 and fractional charge = 0.24. These values are in good agreement with those reported by Sheu et al.[22] and Hollamby et al.[16] The characteristics of the SANS spectra of AOT micelles in NaCl up to 10 mM and in NaSa up to 15 mM are almost similar, and the spectra show strong correlation

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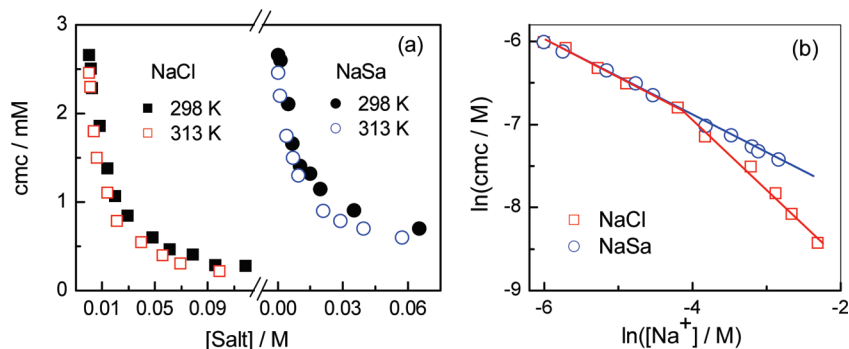(22) Sheu, E. Y.; Chen, S. H.; Huang, J. S. *J. Phys. Chem.* **1987**, *91*, 3306–3310.

Figure 1. (a) Variation of cmc (data at 298 K are from ref 1) and (b) Corrin−Harkins plots of AOT in aqueous NaCl and NaSa solutions with salt concentration at 40 °C.
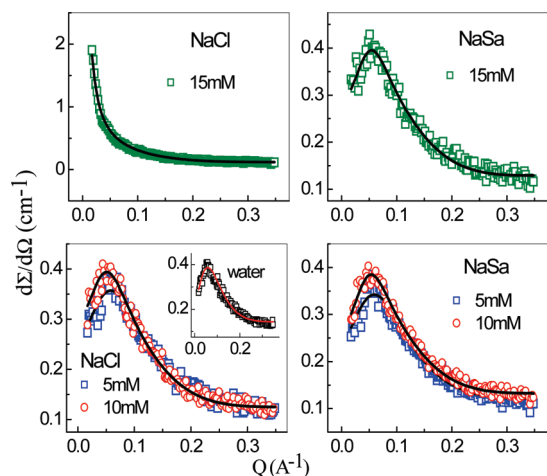

Figure 2. Plots of SANS data (differential scattering cross section per unit volume versus scattering vector) for AOT (15 mM) in water (inset) and aqueous solutions of NaCl and NaSa at 40 °C. Concentrations of NaCl and NaSa are shown in the insets. The lines shown are theoretical fits.

peaks. Compared to the reported SANS profiles of ionic surfactant + salt systems,[23−27] we observed some peculiarities in the SANS spectra of AOT + NaCl/NaSa systems. For e.g., in the SANS spectra of systems like SDS (sodium dodecyl sulfate) + NaCl/PTHC (*p*-toluidine hydrochloride),[23−26] CTAB (cetyltrimethylammonium bromide) + KBr/KCl,[24−26] CTAC (cetyltrimethylammonium chloride) + KBr/KCl,[24−26] and CPC (cetylpyridinium chloride) + NaCl/NaBr[27] by the addition of salts the peak positions shifted to lower Q value due to increase in micellar size and the peaks also broadened due to decrease in micellar charge. On the other hand, in AOT + NaCl/NaSa systems up to 10 mM NaCl and 15 mM NaSa the peak positions remained almost at the same Q value (Figure 2), and consequently aggregation number and axial ratio of AOT micelles derived from the fitting were found to be constant (Figure 3). Moreover, the peaks did not broaden by the addition of NaCl or NaSa. On the contrary, the width of the peaks slightly decreased by the addition of NaCl/NaSa, the decrease in width being relatively more in NaSa. This observation about the width of SANS peaks of AOT
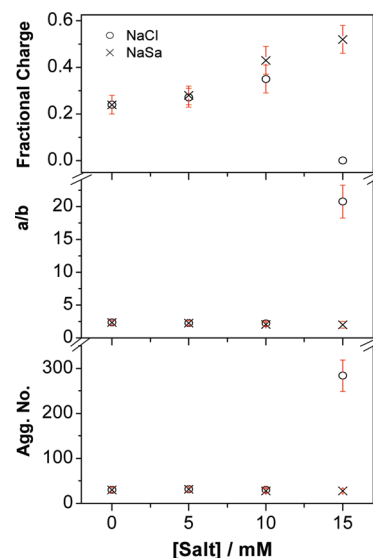
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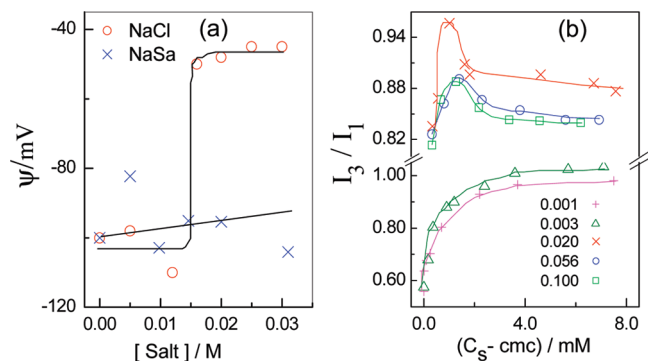
Figure 3. Plots of aggregation number, ratio (a/b) of semimajor to semiminor axes, and fractional charge (from the SANS data fitting) of AOT micelle versus salt concentration at 40 °C. Error bars are shown in red.

micelles is reflected in the fitted values for the fractional charge, which shows an increasing trend with increasing concentration of added salt (Figure 3) unlike the case with the reported systems.[23−27] Interestingly, the correlation peak of AOT micelles disappears in 15 mM NaCl, but not in 15 mM NaSa (Figure 2). In 15 mM NaCl, since there is no correlation peak, the surface charge was fixed as close to zero and the semimajor axis was used as the fitting parameter. The value of axial ratio so obtained clearly indicates that the shape of AOT micelles changes near 15 mM NaCl from prolate spheroid ($a/b \approx 2$; aggregation number ≈30) to rodlike ($a/b \approx 21$; aggregation number ≈280). The values of the factional charge obtained from the SANS data are not in agreement with those determined from CH plots. According to the results from the CH plots and emf data,[1] α should have been (i) about 0.6 in water and in the presence of NaSa and (ii) about 0.6 below 15 mM NaCl and about 0.2 when NaCl concentration is ≥15 mM. However, such expected fractional charge is not obtained from the fitting of SANS data of AOT (Figure 3). Low SANS intensity of AOT micelles hampered obtaining accurate values of fractional charge, axial ratio, and aggregation number from the fitting of SANS data. Nevertheless, from the SANS data of AOT in the absence and presence of NaCl/NaSa it is very clear that (i) the shape of AOT micelles changes when NaCl concentration becomes 0.015 mM, (ii) the shape change of AOT micelles

Figure 4. Variation of (a) zeta potential of AOT micelles in aqueous NaCl and NaSa solutions with salt concentration and (b) I_3/I_1 of pyrene with the amount of AOT that has undergone aggregation in the presence of NaCl (concentrations of NaCl are indicated in the inset) at 40 °C.

does not occur in the presence of NaSa, and (iii) the fractional charge (equal to $1 - \beta$) on the AOT micelle suddenly decreases when its shape changes.

Zeta Potential. To confirm that in the presence of 15 mM NaCl the fractional charge on AOT micelle decreases, we measured zeta potential (ψ) values of aqueous solutions of AOT (concentration = 15 mM) as functions of concentration of NaCl and NaSa at 40 °C (Figure 4a). An abrupt change in ψ near 15 mM NaCl from about −100 to −50 mV, but not in NaSa solution, was observed. The abrupt change in ψ confirms condensation of greater number of counterions into the Stern layer of AOT micelle near 15 mM NaCl, thereby supporting the observation that at this concentration of NaCl a sudden increase in the value of β of AOT takes place.

Fluorescence. The values of the intensity ratio (I_3/I_1) of peak 3 (384 nm) to peak 1 (373 nm) of pyrene fluorescence emission in AOT solution at 40 °C are shown in Figure 4b as a function of $C_s - \text{cmc}$ (C_s is the total surfactant concentration) at fixed NaCl concentrations. From the plots it can be seen that the plot of I_3/I_1 starts passing through a maximum when the concentration of NaCl becomes equal to or greater than 0.02 M, which indicate that near c^* a sudden change in the polarity of the AOT micellar interface occurs. This sudden change in the polarity at the micellar interface is, in turn, indicative of abrupt change in the surface charge of AOT micelle at about 0.02 M NaCl. Since NaSa also shows fluorescence emission in the wavelength range from 375 to 450 nm, we did not measure the intensity ratio of pyrene fluorescence emission in AOT solution in the presence of NaSa.

The dependence of β on the shape of a micelle may be explained as follows: As the concentration of added electrolyte is increased, more counterions bind to a micelle, thereby reducing the repulsion between the head groups at the micellar surface and consequently increasing the aggregation number. Increase in aggregation number increases the size of the micelle, but the value of β remains almost unchanged since it is the ratio of the bound counterions to the aggregation number. However, as the size of the micelle increases, at some point its shape must also change due to geometric factors so as to accommodate the increased number of hydrocarbon tails in the micelle. When such a shape change of the ionic micelle takes place due to geometric constraints, the surface area of micelle per headgroup changes and causes, in turn, a change in the value of β. Thus, the value of β does not change due to increase in the size of ionic micelle until the micellar shape changes. Change of β due to micellar shape change was proposed by Fujio et al.,[16] who also reported that β of ionic micelles increase in the order of sphere < oblate ellipsoidal < rodlike.
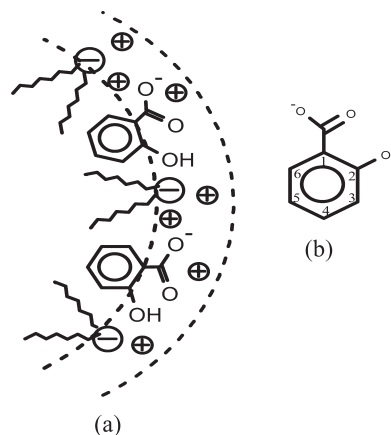

(a)

Figure 5. (a) Schematic representation of the binding of salicylate coanion at the AOT micelle−water interface. (b) Structure of salicylate ion.

The difference in the counterion binding behavior of AOT in aqueous NaSa solution compared to that in NaCl solution may be explained due to the binding of salicylate coanion to AOT micelle. In spite of possessing negative charge, salicylate ion can still bind to the anionic AOT micelle due to (i) hydrophobic interactions between the phenyl ring of salicylate and water, (ii) short-range van der Waals interactions between hydrocarbon tails of AOT and phenyl ring of salicylate, and (iii) shielding of electrostatic repulsive interactions between the negatively charged head groups of salicylate and AOT due to hydration. The binding of salicylate ion to AOT micelle is similar to the binding of SDS to AOT during the formation of their mixed micelle. A schematic diagram of salicylate binding to AOT micelle is shown in Figure 5a. Because of the salicylate binding, the effective surface charge of AOT micelle becomes more and hence no change in micellar shape and increase in β occur in aqueous NaSa solution.

To ascertain the binding of salicylate coanion to AOT micelle and its position in the micelle, we performed proton NMR measurements of neat NaSa and NaSa in the presence of AOT. The NMR spectra are shown in Figure S1. In the presence of AOT micelle, the chemical shift values of protons in the 3-, 4-, 5-, and 6-positions of salicylate (Figure 5b) are lowered by 0.074 ± 0.001 ppm (Figure S1), suggesting nonpolar environment of these protons. A similar lowering of chemical shift values of the protons of salicylate bound to CTAB cationic micelle was reported by Rao et al.[28] Thus, NMR spectra confirm the binding of salicylate coanion to the AOT micelle as visualized in Figure 5a.

Conclusions

SANS profiles of AOT in the presence of NaCl clearly reveal a change in the shape of AOT micelle near the NaCl concentration where a 2-fold increase in its β value occurs. From the SANS data analysis this shape change has been shown to be from prolate spheroid to rodlike shape. On the other hand, SANS profiles of AOT in the presence of NaSa do not indicate any shape change of AOT micelle, and interestingly in NaSa solution no abrupt change in the value of β also occurs. Therefore, it can be concluded that counterion binding constant of ionic micelle is a micellar shape dependent parameter. From the present study it can be proposed that β of prolate ellipsoidal shaped micelle is less than that of rodlike-shaped micelle. This is consistent with the proposition made by Fujio et al.[15] that the values of β follow the order spherical < oblate ellipsoidal < rodlike micelle.

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Generally, the counterion binding is thought to be one of the factors determining size and shape of ionic micelles. It emerges from this study that counterion binding controls the size of micelles, but shape change occurs due to geometrical requirement. Since a shift in the value of β takes place as the micellar shape changes, surface charge density (ratio of micellar charge to its surface area) rather than surface charge appears to control β. This concept can be applied to explain why sodium deoxycholate (bile salt) micelle has very low value of β. Sodium deoxycholate due to formation of facial micelle[29] has low surface charge (low aggregation number) and large surface area resulting in low surface charge density and hence low β value.

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Supporting Information Available: Results of SANS fitting (Table S1), ^{1}H NMR spectra of NaSa in the absence and presence of AOT (Figure S1), and more details of experimental measurements. This material is available free of charge via the Internet at http://pubs.acs.org.