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Effect of ethylene glycol on the special counterion binding and microstructures of sodium dioctylsulfosuccinate micelles

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ABSTRACT

Sodium dioctylsulfosuccinate (AOT) micelle has a special counterion binding behavior (SCB), which refers to the abrupt twofold increase in the counterion binding constant (β) at a critical concentration (c^*) of added NaCl (in water $c^* \approx 0.015$ mol kg^{-1}). In this paper, the SCB of AOT has been studied in a mixture of water and ethylene glycol (EG) by applying surface tension, fluorescence, and small angle neutron scattering (SANS) methods. The SCB exists in water + 10% (w/w) EG as well, but disappears when the EG% is $\geqslant$20. It has been found out that the SCB of AOT occurs in media having cohesive energy density values in the range of 2.3–2.75 J m^{-3}. SANS data indicate co-existence of vesicles and cylindrical micelles of AOT in water + 10% EG when the added NaCl concentration is greater than c^* thereby revealing that change in the morphology of aggregated species is the probable cause for the SCB of AOT. From this study it has become clear that the Corrin–Harkins (CH) equation, commonly used for determining β, can be applied only above a limiting concentration ($c_e^{\#}$) of added electrolyte. In aqueous organic or pure organic polar solvents below $c_e^{\#}$ sharp deviation from the CH equation occurs with reversal of slope rendering this equation inapplicable for the determination of β.

1. Introduction

As aggregation of amphiphilic molecules is a solvent – induced phenomenon, investigating the aggregation process of surfactants in solvents of varying polarity is considered to throw light on fundamental aspects of aggregation behavior of amphiphiles. Moreover, tuning the aggregation process as well as the characteristics of the aggregated species is possible by adjusting the composition of a mixed solvent medium. These viewpoints have led to reprising the study on the aggregation of surfactants in different solvent media time and again, which is reflected in the papers published in recent past [1–18]. Besides solvents, counterions play important role in inducing structural or shape transitions of surfactant aggregates. Some of the applications of ionic micelles, e.g., as drug delivery system, are attributed to the occurrence of structural changes in micelles (such as transition from micelle to vesicle). It is therefore important to understand the counterion binding behavior of ionic micelles in mixed solvents. In the studies on the aggregation of surfactants in mixed solvents, the attention paid to the binding behavior of counterions to ionic micelles, particularly in the light of the thermodynamic approach developed by Corrin and Harkins [19], is however quite limited [20].

Sodium dioctylsulfosuccinate (AOT), a double-chained anionic surfactant, is known for its special features [21–23]. One of the recently reported [22,23] special features of AOT is its special counterion binding behavior (SCB), viz., the counterion binding constant (β) value of AOT suddenly doubles (from about 0.4 to 0.8) in the presence of about 0.015 mol kg^{-1} NaCl in aqueous medium. The small angle neutron scattering (SANS) measurements [23] revealed that the shape change of AOT micelle is responsible for the SCB of AOT. In order to obtain further insight into the SCB of AOT, it is interesting to study the effect of solvent on the SCB. An earlier study [5] in water + propylene carbonate (PC) media has indicated the dependence of the SCB of AOT on solvent, but this study was limited to only 18 wt.% PC due to miscibility problem.

In the present study, we chose water + ethylene glycol (EG) mixtures to study the effect of solvent on the SCB of AOT. EG is an important solvent due to its large applications in industry and cryobiology [24–26] and it has got complete miscibility with water. It has been reported [4] recently that in water + EG mixed solvent AOT undergoes hydrogen bonding with the solvent molecules and therefore it is important to explore whether this hydrogen bonding has any influence on the SCB. For these reasons, we considered water + EG to be an interesting mixed solvent

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medium. Surface tension, fluorescence and SANS methods were employed for the characterization of SCB in the present study.

2. Materials and methods

AOT (Sigma, 99% assay) and sodium chloride (Merck, 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. For SANS measurements D_2O (99.9 atom% D) was used. Surface tension measurements were made by using a K11 Krüss tensiometer and Wilhelmy plate. Before every use, the plate was first rinsed with acetone to remove any organic material sticking to the plate and thereafter washed with Millipore water. Finally, the plate was heated to red hot with a Bunsen burner and then cooled. Fluorescence emission intensities of probe molecule in the experimental medium were recorded using a Hitachi F4500 FL spectrophotometer. Pyrene (Fluka, >97%) was used as a probe. SANS measurements were performed at SANS-I facility, Swiss Spallation Neutron Source SINQ, Paul Scherrer Institut, Switzerland [27]. The wavelength (λ) of neutron beam was 6 Å and the scattered neutrons from samples were detected using two-dimensional 96 cm × 96 cm detector. Data were collected at two sample-to-detector distances (2 and 8 m) to cover a wave vector transfer ($Q = 4\pi\sin(\theta/2)/\lambda$, where θ is scattering angle) range of 0.008–0.3 $Å^{-1}$. In SANS measurements for a particular composition of D_2O + EG, the concentration of AOT was kept fixed and the concentration of NaCl was varied. The samples were held in HELLMA quartz cells having thickness 1 mm and temperature were kept fixed at 25 °C. The measured SANS data were corrected for the background, the empty cell contributions, and normalized to absolute cross-sectional unit using standard protocols.

3. Results and discussion

3.1. Surface tension

Surface tension (γ) plots of AOT solution in water + EG media (EG amount = 10% and 80% by weight) with varying amounts NaCl are shown in Fig. 1. Similar surface tension plots of AOT in 20%, 30%, 40%, 50%, 60%, 70%, 90% and 100% EG are shown in Figs. S1–S4. The break in the surface tension plot corresponding to the cmc shifts to lower surfactant concentration when the amount of NaCl in the medium increases indicating the lowering of cmc with increase in NaCl concentration. On the other hand, the premicellar surface tension break occurring in solutions containing 60% or more EG (Figs. 1 and S1–S4) tends to vanish gradually or becomes less and less pronounced with increasing amount of NaCl. As reported recently [4], this premicellar surface tension break is due to hydrogen bonding between water, EG and AOT and it tends to disappear eventually by adding NaCl because of the tendency of added electrolyte to weaken the hydrogen bonding [28].

The values of cmc obtained from the surface tension plots are listed in Tables S1–S3 and also shown in Fig. 2. The cmc values of AOT in water as a function of NaCl concentration were taken from our previous study [22].

3.2. Fluorescence

An attempt was made to determine the cmc as a function of NaCl in water + EG media by the fluorescence technique using pyrene as the probe. The representative plots of I_1/I_3 ratio of pyrene as a function of AOT concentration in water + 10% EG containing different amounts of NaCl are shown in Fig. 3 and similar plots in other compositions of water + EG are shown in Figs. S5–S6. I_1 and I_3 refer to the intensities of the fluorescence emission spectra of pyrene at 374 and 384 nm, respectively. Applying the method of Aguiar et al. [29] to estimate cmc, we fitted the I_1/I_3 data to the sigmoidal equation

$$I_1/I_3 = A_2 + \{(A_1 - A_2)/[1 + \exp((c_s - x_0)/b_0)]\} \tag{1}$$

where c_s represents AOT concentration, x_0 is the value of c_s corresponding to the center of the sigmoid, A_1 and A_2 are the upper and lower limits of the sigmoid, respectively, and b_0 is a term that reflects the range of c_s where sudden change in I_1/I_3 occurs. The values of the parameters of Eq. (1) obtained from the fitting are listed in Table S4 and the value of x_0 is taken as cmc. As the amount of EG increases the agreement between x_0 and the cmc obtained from the surface tension becomes poor. Earlier studies have also revealed that the value of x_0 does not always match with the cmc [29,30]. Thus, cmc values estimated from the fluorescence technique become less reliable when the EG amount in the mixture is about 50% or more, because population of pyrene in the bulk increases with increasing EG amount in the mixture.

3.3. Counterion binding constant

Counterion binding constant (β) of an ionic surfactant is determined from the well known Corrin–Harkins (CH) equation [19]

$$\ln c_0 = A - \beta \ \ln(c_0 + c_e) \tag{2}$$

where c_0 and c_e represent cmc and electrolyte concentration, respectively. The sum $c_0 + c_e$ is equal to the total concentration of

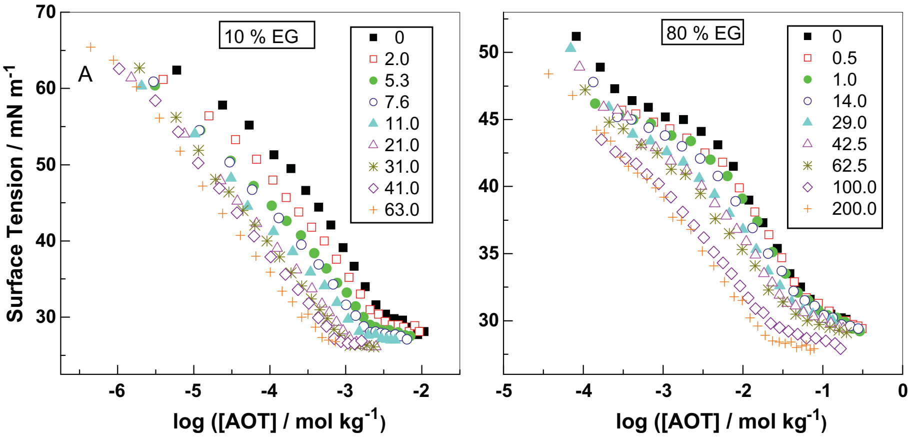

Fig. 1. Surface tension isotherms of AOT in 10% and 80% EG containing different amounts of NaCl. Concentrations of NaCl in mmol kg^{-1} are shown in the inset.