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Aggregation and adsorption of sodium dioctylsulfosuccinate in aqueous ammonium chloride solution: Role of mixed counterions

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ABSTRACT

The critical micelle concentration (cmc) of sodium dioctylsulfosuccinate (AOT) was determined at 25 °C from surface tension and fluorescence methods in aqueous NH_4Cl solution for assessing the influence of mixed counterions on the special counterion binding behavior (SCB) of AOT. The SCB of AOT refers to a sudden twofold increase in the value of the counterion binding constant (β) in aqueous medium when the concentration (c^*) of the added 1:1 sodium salt is about 0.015 mol kg^{-1}, and it has been tested so far for sodium ion only. In the presence of sodium and ammonium mixed counterions also the SCB of AOT exist, but with lower c^* (0.009 mol kg^{-1} NH_4Cl). Synergism in the cmc occurs due to mixed counterions. In the case of inorganic counterions, unlike the case with organic counterions, the cmc is dependent on the total counterion concentration in solution and negligibly on the specific type of counterion. Na^+ and NH_4^+ bind almost equally to the micelle in the region of low β (below c^*), but in the region of high β (above c^*) NH_4^+ binds predominantly. It has been shown that the theoretical expression for the surface excess of ionic surfactant + electrolyte system containing a single counterion can also be used to evaluate the surface excess in the presence of mixed counterions if the two counterions are considered to undergo Henry-type adsorption at the air–solution interface.

1. Introduction

Sodium dioctylsulfosuccinate (AOT) has a special counterion binding behavior (SCB) [1–4], viz. the value of its counterion binding constant (β) undergoes a sudden twofold increase in aqueous NaCl solution. It has been established that shape change of AOT micelle is responsible for the abrupt change in β [4]. AOT, which is considered to be a special surfactant [5–8], is perhaps the only anionic surfactant whose micelle undergoes a shape change in aqueous medium at a very low concentration (around 0.015 mol kg^{-1}) of added sodium ion, since in other anionic surfactants, micellar shape change occurs at low concentration of electrolyte only if the added counterion is multivalent [9–13]. It is also reported [4] that organic coion like salicylate has suppressing effect on the sudden increase in the value of β of AOT.

Although AOT-type surfactants with different counterions were synthesized and studied [14–17], the SCB of AOT is yet to be tested for counterions other than sodium and for mixed counterions. Therefore, our main interest is to examine how the SCB of AOT is influenced by the nature of counterions. With this objective in mind, we measured in the present work surface tension of AOT in aqueous NH_4Cl solution as this system contains a mixture of Na^+ and NH_4^+ counterions. The fluorescence emission method was also used to check the critical micelle concentration (cmc) values of AOT in the presence of NH_4Cl.

2. Materials and methods

AOT (Sigma, 99% assay), NH_4Cl (sd fine chemicals, 99.8% assay), NaCl (Merck, 99.5% assay), and pyrene (Fluka) 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. Surface tension measurements were taken by the Wilhelmy plate method using a Krüss K11 tensiometer attached with a thermostat (Haake DC 10). The fluorescence emission spectra of pyrene were recorded using Hitachi F4500 FL spectrophotometer. The details of solution preparation, surface tension measurement, and fluorescence emission intensity measurement are given in our earlier papers [1,18]. All measurements were taken at 25 °C.

3. Results and discussion

3.1. Surface tension, fluorescence emission, and critical micelle concentration

The plots of surface tension (γ) versus log[AOT] corresponding to aqueous NH_4Cl solutions of different concentrations are shown

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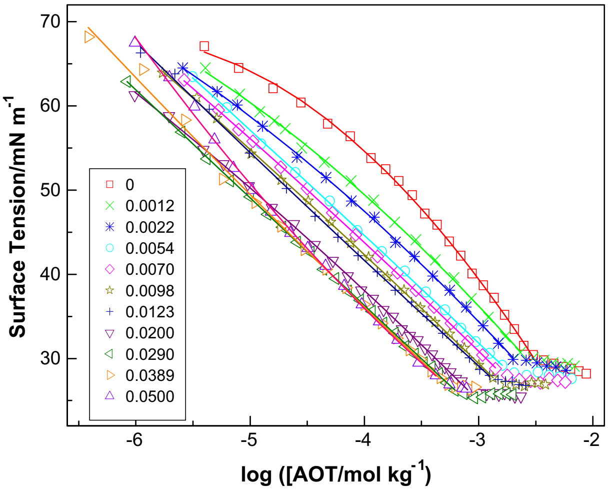

Fig. 1. Variation of surface tension of aqueous AOT + NH_4Cl solution with AOT concentration. The molal concentrations of NH_4Cl are indicated in the inset. The lines represent the surface tension values calculated by the polynomial fitting of the experimental data below cmc.

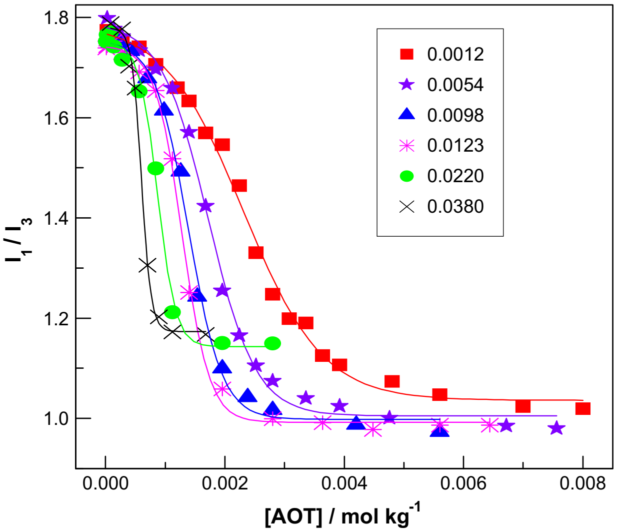

Fig. 3. Variation of I_1/I_3 of pyrene with AOT concentration in aqueous NH_4Cl solutions. The molal concentrations of NH_4Cl are indicated in the inset.

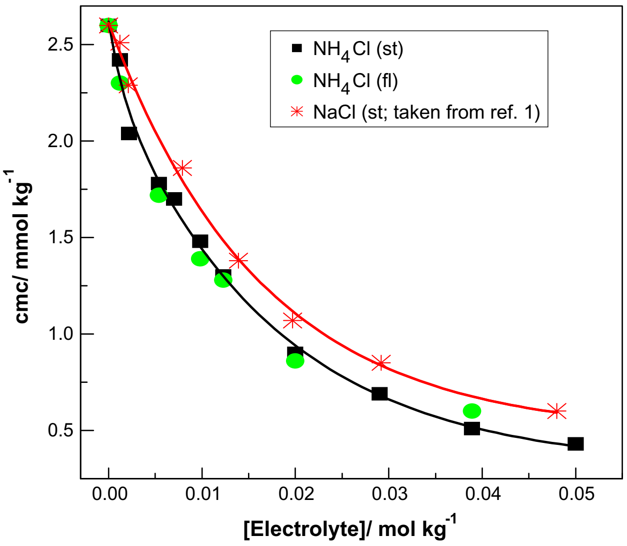

Fig. 2. Variation of cmc of AOT with added electrolyte concentration at 25 °C. 'st' and 'fl' indicate that cmc values are from surface tension and fluorescence data, respectively.

in Fig. 1. Due to low solubility of AOT in NH_4Cl, the present study has been restricted up to 0.05 mol kg^{-1} of NH_4Cl. The values of cmc determined from the surface tension isotherms are listed in Table S1 and also shown in Fig. 2. The present cmc value (2.60 mmol kg^{-1}) of AOT is close to the reported [15–17,19,20] values.

The cmc has also been determined by the fluorescence technique by using pyrene as the probe. The I_1/I_3 ratio of pyrene was plotted as a function of AOT concentration as shown in Fig. 3. To determine cmc from the I_1/I_3 data, we adopted the approach reported by Aguiar et al. [21], and accordingly, the plots given in Fig. 3 were fitted to a sigmoid type equation of the form

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

In Eq. (1), 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 S1. Aguiar et al. [21] concluded on an empirical basis that cmc = $x_0 + 2b_0$ and $x_0/b_0 > 10$ for ionic surfactants, whereas cmc = x_0 and $x_0/b_0 < 10$ for nonionic surfactants. In the present case, it is observed that cmc of AOT (obtained from γ) is close to x_0 and $x_0/b_0 < 10$, which according to Aguiar et al. [21] are characteristics of nonionic surfactants. Thus, parameters of Eq. (1) are strongly dependent on the nature of the surfactant and medium as reported in SDS + acetamide system [22] also.

In Fig. 2, we have compared the cmc values of AOT in NH_4Cl solutions with those in NaCl solutions [1], and it is apparent from Fig. 2 that the cmc of AOT is higher in aqueous NaCl solutions. Therefore, the mixture of NH_4^+ and Na^+ reduces the cmc of AOT more than Na^+ alone. The cmc of NH_4-AOT (ammonium dioctylsulfosuccinate) has been reported as equal to 2.70 mmol kg^{-1} by Saha and coworkers [15,16] and 3.01 mmol kg^{-1} by Eastoe and coworkers [17] (at this low concentration, mol dm^{-3} is considered to be almost equal to mol kg^{-1}). Therefore, sodium and ammonium counterions affect almost equally the critical concentration at which dioctylsulfosuccinate micellizes. Consequently, the cmc values of AOT in NH_4Cl solutions are expected to be slightly higher than or equal to those in NaCl solutions. On the contrary, the cmc values of AOT in NH_4Cl solutions are lower than those in NaCl solutions (Fig. 1). Therefore, it is interesting to note that with respect to AOT, the cmc lowering effect of NH_4^+ in the presence of Na^+ is more than that of Na^+ alone. This reveals that synergism occurs in the cmc retarding ability of counterions when they are in the mixed form. The synergistic effect is quantified in terms of interaction parameter, which in turn is related to the free energy of micelle formation [23]. The free energy of micelle formation has several contributions, and out of these, the electrostatic contribution due to repulsive interaction between head groups is positive, which decreases due to the binding of counterions thereby favoring micellization as reflected by the depression in cmc [23–25]. The shielding of the interaction between head groups by the bound counterions is dependent on their size and charge. When mixed counterions of different sizes bind to an ionic micelle, the effective shielding may not be simply additive thereby causing synergism in cmc.

3.2. Counterion binding constant

The counterion binding constant (β) of an ionic surfactant is commonly determined by using the well-known Corrin–Harkins (CH) equation, which is of the form

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

where A is a constant related to the standard free energy of micellization, c_0 is the cmc, and c_e is the concentration of the added electrolyte. Eq. (2) was derived for the case of ionic surfactant solutions containing added electrolyte with the same counterion as that of the surfactant. The system studied here contains mixed counterions, viz. NH_4^+ and Na^+, and hence theoretically, Eq. (2) is not applicable to such a system. In fact, in one of our recent studies [18] on aqueous systems containing CPC + NaSa/NaBz (CPC: cetylpyridinium chloride; NaSa: sodium salicylate; NaBz: sodium benzoate), we have shown that when the CH equation was applied to this mixed counterions system a sharp deviation from Eq. (2) occurred in the low concentration region of electrolyte, and the deviation was so much that the slope of the CH plot became positive instead of negative. Such a deviation was, however, not observed in the CH plot (Fig. 4A) of the present mixed counterions system, and instead, the nature of the CH plot is similar to that of AOT + aqueous NaCl system [1]. This demonstrates that cmc of AOT in aqueous medium in the presence of 1:1 inorganic salts depends mostly on the total counterion concentration (C) and very less on the specific type of the cationic counterions present in the solution. We can therefore write Eq. (2) in an empirical form as

$$\ln c_0 = A_e - \beta_e \ln C \tag{3}$$

The terms A_e and β_e are considered as empirical constants. It may be noted that when the added electrolyte is of 1:1 type and contains same counterion as that of the surfactant, then Eqs. (2) and (3) become identical with $A_e = A$ and $\beta_e = \beta$. Alargova et al. [9–12] studied the micellization of sodium dodecyl dioxyethylene sulfate (SDDS) in aqueous medium in the presence of $NaCl/AlCl_3$ and expressed the variation of cmc with $NaCl/AlCl_3$ concentration using an expression similar to Eq. (3) wherein they used ionic strength (I) term in place of C. The terms I and C are, however, equal when the added electrolyte is of 1:1 type. By comparing the plot of Eq. (3) for AOT + NH_4Cl (Fig. 4A) with that reported for AOT + NaCl solution [1], by analogy we can conclude that shape change of AOT micelle takes place in aqueous NH_4Cl solution also as in the case of NaCl, but at a lower electrolyte concentration equal to 0.009 mol kg^{-1}. Thus, plots based on Eq. (2), (3) exhibit different linear regions depending upon the shape of the ionic micelle. In SDDS + NaCl + $AlCl_3$ system, Alargova et al. [9–11] reported micellar shape transition from sphere to cylinder and their observation that the plot of lnc_0 versus ln$I$ was linear in a chosen range of ionic strength corresponding to the region of cylindrical micellar shape also supports the view that graphical representation of Eq. (2), (3) falls on different linear regions if the micellar shape changes within the chosen range of electrolyte concentration. The β_e values obtained from Fig. 4A for the AOT + NH_4Cl system are 0.37 and 0.84, which are in close agreement with the β values reported [1] for AOT + NaCl system. The ionic size [26,27] of NH_4^+ is higher than that of Na^+, and both these ions have approximately same hydration numbers (4 or 5) [28,29]. Therefore, due to binding of NH_4^+, the surface area of the AOT micelle increases causing increase in the surface area-to-volume ratio of the micelle, which may be responsible for a transition from prolate to cylindrical shape of AOT micelle [4] at a lower concentration of NH_4Cl.

As mentioned above, theoretically Eq. (2) is not applicable to ionic surfactant solutions containing mixed counterions. We recently [18] proposed a modified form of the CH equation that was successfully applied to CPC + NaSa/NaBz systems, which is of the form

$$\ln c_0 = A' - B \ln c_e \tag{4}$$

where $A' = \Delta G_m^0/[(1+\beta_1)RT]$ and $B = \beta_2/(1+\beta_1)$. ΔG_m^0 is the standard free energy of micellization per mole of ionic surfactant. β_1 and β_2 are the counterion binding constants for Na^+ and NH_4^+, respectively and $\beta = \beta_1 + \beta_2$. Thus, we get a modified theoretical form of the CH equation for surfactant systems containing mixed counterions. Eq. (4) is applicable only when $c_e > 0$ and the added electrolyte contains counterion different from that in the surfactant molecule. It is interesting to note that the CH equation becomes similar to the modified CH equation in the high concentration region of electrolyte where $c_e \ll c_0$ so that $c_0 + c_e \approx c_e$. However, the modified CH Eq. (4), unlike the CH Eq. (2), does not give the value of β directly from the slope. An attempt has been made to apply Eq. (4) to the present system under investigation by plotting lnc_0 versus lnc_e in Fig. 4B. From Fig. 4B, it can be seen that the modified CH plot also falls on two linear regions, which is similar to the nature of the CH plot of AOT in aqueous NaCl solution [1] as well as to the nature of the plot (Fig. 4A) corresponding to Eq. (3). The change over in the value of the slope of the plot in Fig. 4B takes place at [NH_4Cl] ≈ 0.009 mol kg^{-1} (c^*), which coincides with that observed from Fig. 4A also. The least-squares fitted values of the parameters of Eq. (4) are $A' = -7.34$, $B = 0.19$ below c^* and $A' = -10.05$, $B = 0.77$ above c^*. Since B is related to the two counterion binding constants, a sudden change in the value of B at c^* implies sudden changes in the values of β_1 and β_2. The two values of B indicate that β must be more than 0.19 below c^*, and it must be more than 0.77 above c^* (otherwise $\beta_2 > \beta$,

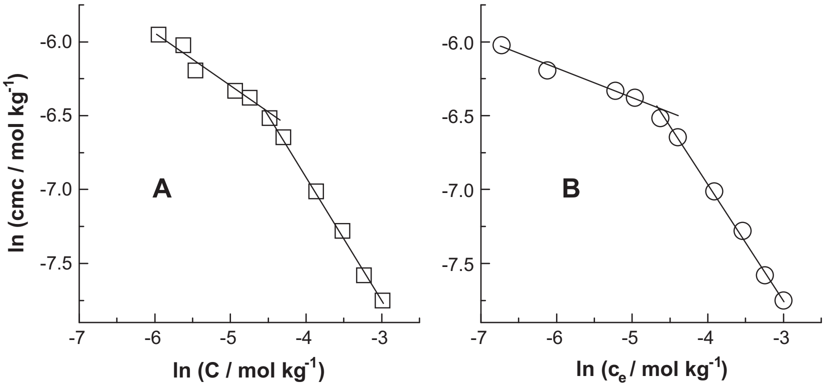

Fig. 4. Plots of (A) Eq. (3) and (B) Eq. (4) for aqueous solutions of AOT + NH_4Cl.

which is not allowed). Therefore, at c^*, the values of β, β_1, and β_2 suddenly change, and this may be attributed to the shape change of AOT micelle that may be anticipated to occur at c^* as described above. Presuming β_e as almost equal to β, we get $\beta_1 = 0.15$ and $\beta_2 = 0.22$ below c^* and $\beta_1 = 0.04$ and $\beta_2 = 0.80$ above c^*. Thus, above c^*, majority of the counterions bound to the micelle are NH_4^+, which is most probably the cause of shape change due to the increase in surface area-to-volume ratio of the micelle. The present study establishes that the special counterion binding behavior of AOT exists in the presence of mixed counterions also.

3.3. Free energy

The standard free energy of micellization per mole of ionic surfactant has two components and is written as $\Delta G^0_{\mathrm{m}} = \Delta G^0_{\mathrm{hc}} + \Delta G^0_{\mathrm{el}}$. $\Delta G^0_{\mathrm{hc}} = \mathrm{RT}\ln X_{\mathrm{cmc}}$ is the standard free energy change due to the transfer of one mole of hydrocarbon chain with head group from the bulk to the micellar phase. $\Delta G^0_{\mathrm{el}} = \beta \mathrm{RT}\ln X_{cmc}$ is the standard free energy change due to the transfer of counterions from the bulk to the micellar interface. Considering $\beta_e \approx \beta$ as stated above, we calculated the values of ΔG^0_{m}, ΔG^0_{hc}, and ΔG^0_{el}. A plot showing the variation in ΔG^0_{m} with the concentration of electrolyte is shown in Fig. 5. For comparison, the values of ΔG^0_{m} for AOT + NaCl [1] are also shown in Fig. 5. It is clear from the plot that mixed counterions have a favoring effect on the micellization of AOT. The sudden decrease in ΔG^0_{m} at c^*, which is not there in ΔG^0_{hc}, is due to the sudden shift in the value of β.

3.4. Surface excess

In the presence of an added 1:1 electrolyte XC_1, which contributes same counterion as that of the surfactant molecule (also 1:1 type), and presuming electroneutrality of the adsorbed layer, the relation for the surface excess at the cmc (Γ_{cmc}) is of the form [30]

$$\Gamma_{\mathrm{cmc}} = -\frac{1}{RT}\left[\frac{1}{1+\frac{c_0}{c_0+c_e}}\right]\left(\frac{\mathrm{d}\gamma}{\mathrm{d}\ln c_s}\right)_{c_e,c_s\to c_0} \qquad (5)$$

On the other hand, if the added 1:1 electrolyte is XC_2, where counterion C_2 is different from the counterion C_1 of the surfactant molecule, then the expression for Γ in the presence of mixed counterions takes the form [18]:

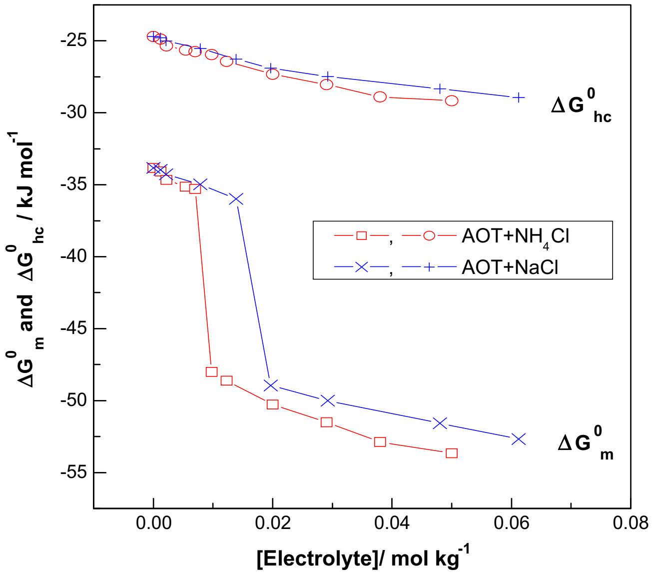

Fig. 5. Variation of ΔG^0_{m} and ΔG^0_{hc} of AOT with concentration of NH_4Cl and NaCl (data from Ref. [1]).

$$\Gamma_{\mathrm{cmc}} = -\frac{1}{\mathrm{RT}(1+\beta_{1\mathrm{ad}})}\left(\frac{\mathrm{d}\gamma}{\mathrm{d}\ln c_s}\right)_{c_e,c_s\to c_0} \qquad (6)$$

while deriving Eq. (6), the adsorption of the coion X^- has been neglected and the adsorption layer is treated as electroneutral by imposing $\beta_{\mathrm{ad}} = \beta_{1\mathrm{ad}} + \beta_{2\mathrm{ad}} = 1$. $\beta_{1\mathrm{ad}} = \Gamma_{c1}/\Gamma$ and $\beta_{2\mathrm{ad}} = \Gamma_{c2}/\Gamma$ are the binding constants for the native (C_1) and foreign (C_2) counterions, respectively. Although Eq. (6) is an exact theoretical expression for the surface excess of ionic surfactants in the presence of mixed counterions, its application is hampered due to nonavailability of actual values of $\beta_{1\mathrm{ad}}$ or $\beta_{2\mathrm{ad}}$. To overcome this problem in employing Eq. (6), we adopted the following treatment: For a chosen value of β_{ad}, the value of $\beta_{2\mathrm{ad}}$ will vary depending upon the concentration of NH_4Cl. We presume that the counterions obey Henry's adsorption isotherm (limiting Langmuir's adsorption isotherm) near the cmc. Theoretical modeling of adsorption in aqueous SDS + NaCl system done by Kralchevsky and coworkers [31,32] indicates for counterions near the cmc, in fact, adsorption similar to Henry's type isotherm. We can therefore write $\beta_{1\mathrm{ad}} \approx K_{1\mathrm{ad}}c_s$ and $\beta_{2\mathrm{ad}} \approx K_{2\mathrm{ad}}c_e$. Further, the adsorption coefficients $K_{1\mathrm{ad}}$ (for Na^+) and $K_{2\mathrm{ad}}$ (for NH_4^+) are treated to have approximately same value, which is justified by the observation that AOT + NH_4Cl and AOT + NaCl solutions corresponding to a particular concentration of electrolyte have almost same surface tension near the cmc. We then get $\beta_{1\mathrm{ad}}/\beta_{2\mathrm{ad}} \approx c_0/c_e$, which provides us the relation:

$$\beta_{1\mathrm{ad}} = c_0/(c_0 + c_e). \qquad (7)$$

It is interesting to note that by substituting the value of $\beta_{1\mathrm{ad}}$ given by Eq. (7) in Eq. (6) we get the same relation for Γ_{cmc} as that given by Eq. (5). This finding enables us to evaluate from Eq. (5) the surface excess of AOT in the presence of Na^+ and NH_4^+ counterions without knowing the values of $\beta_{1\mathrm{ad}}$ or $\beta_{2\mathrm{ad}}$. It may be noted that Eq. (5) is applicable to compute the surface excess in the electroneutral adsorbed layer of ionic surfactants under the influence of single as well as mixed counterions, but the significance of the term $c_0/(c_0 + c_e)$ in Eq. (5) is different in the two cases. (i) In the presence of mixed counterions, $c_0/(c_0 + c_e)$ term accounts for the number of native counterions bound per adsorbed monomer of the surfactant ($\beta_{1\mathrm{ad}}$) under the assumption that counterions obey Henry's adsorption isotherm. (ii) On the other hand, in the presence of single counterion, $c_0/(c_0 + c_e)$ term appears in Eq. (5) due to the contribution of added electrolyte to the concentration of the native counterion in the solution, and more specifically, this term emerges while transforming $\mathrm{d}\ln(c_s + c_e)$ into $\mathrm{d}\ln c_s$ at the cmc and at constant c_e.

To evaluate Γ_{cmc} of AOT in the presence of Na^+ and NH_4^+ counterions from Eq. (5), the values of the slope $\mathrm{d}\gamma/\mathrm{d}\ln c_s$ at the cmc in different NH_4Cl solutions were determined by fitting the surface tension data below cmc to a polynomial as shown in Fig. 1. The values of Γ_{cmc} of AOT thus obtained are presented in Fig. 6 as a function of NH_4Cl concentration. The values of Γ_{cmc} determined separately by using concentration and activity (mean activity coefficients calculated from the Debye–Hückel limiting law [18] were used to convert concentration to activity) differed to a maximum extent of ±2%. Γ_{cmc} attains limiting value ($\sim 2.2 \times 10^{-6}$ mol m^{-2}) at about 0.025 mol kg^{-1} NH_4Cl, whereas in NaCl solution Γ_{cmc} of AOT is reported [1] to attain the limiting value ($\sim 2.4 \times 10^{-6}$ mol m^{-2}) at about 0.06 mol kg^{-1} NaCl. Higher ionic radius of NH_4^+ compared with that of Na^+ seems to be responsible for higher surface area per mole of adsorbed AOT in NH_4Cl solution and also for saturation of adsorbed layer at lower NH_4Cl concentration.

It is pertinent to comment here about the determination of surface excess from the Gibbs equation. The Gibbs equation can be written for a 1:1 type ionic surfactant like AOT in the absence of any added electrolyte as:

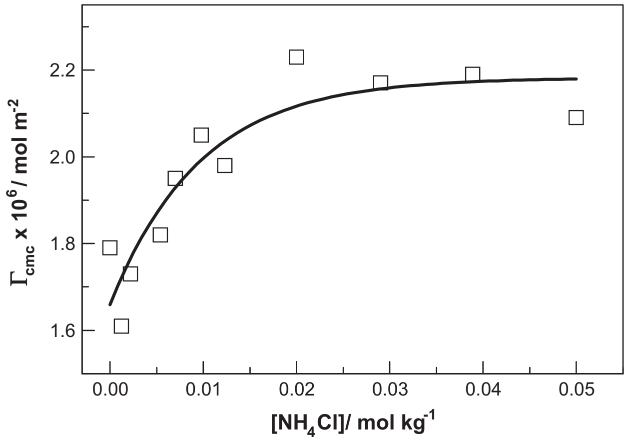

Fig. 6. Surface excess of AOT at 25 °C in aqueous medium in the presence of NH_4Cl calculated from Eq. (5).

$$\Gamma = -\frac{1}{\mathrm{mRT}}\left(\frac{\mathrm{d}\gamma}{\mathrm{dlnc}_s}\right). \qquad (8)$$

Eqs. (5) and (6) correspond to different forms of the Gibbs equation for ionic surfactant + electrolyte systems. In Eq. (8), the factor m has a value 2, which is also evident from Eq. (5) when $c_e = 0$. It was reported by Thomas and coworkers [33,34] and also by Eastoe and coworkers [35,36] that the value of m had to be adjusted (less than 2) to have agreement between the Γ values determined from the neutron reflectivity and surface tension measurements when the surfactant sample contained impurities. In the case of AOT, trace amounts of Ca^{2+} impurity was reported [34,36] to be responsible for lower values of Γ. However, values of Γ from surface tension agreed ($m = 2$) with that from neutron reflectivity if small amount of tetrasodium ethylenediaminetetraacetate (EDTA) is added to AOT as EDTA removes Ca^{2+} from the interface [34,36]. In the present case, for AOT, we found that $\Gamma_{cmc} = 1.79 \times 10^{-6}$ mol m^{-2} (area per molecule at the cmc = 93 Å^2), whereas the value reported [34] from neutron reflectivity is 2.12×10^{-6} mol m^{-2} (area per molecule at the cmc = 78 Å^2). Therefore, the values of Γ_{cmc} presented in Fig. 6 are expected to be about 15% lower due to probable surfactant impurities.

4. Conclusions

This study has shown that the SCB of AOT exists in aqueous NH_4Cl solution. Therefore, it can be concluded that the SCB of AOT is not limited to sodium counterion, but can exist in the case of other counterions also and the value of c^* is dependent on the nature of counterions.

An interesting inference from the present study is that synergism in the cmc of AOT occurs when the solution contains a mixture of sodium and ammonium counterions. Although synergism in cmc due to mixing of two different surfactants is well known, that due to mixed counterions is a relatively less highlighted phenomenon. The present study prompts many questions as to what would happen if one of the mixed counterions is a larger inorganic ion or an organic ion with hydrophobic effect. It would therefore be interesting to take up the study of counterion binding behavior of AOT in aqueous solutions of tetraalkylammonium (TAA) salts. The preliminary results of this study carried out in our laboratory indicate that synergism in cmc is more than in ammonium chloride solution and it increases with increase in the length of the alkyl chain of TAA ion.

It has been shown that when the system contains ionic surfactant with mixed inorganic counterions, the CH equation can still be used as an empirical equation since cmc of such system depends mostly on the total counterion concentration and very less on the specific type of the counterions. This particular observation of this study is different from what was noticed in ionic surfactant system containing organic ion as one of the mixed counterions, e.g., in the case of CPC + sodium salicylate/benzoate [18]. A new approach for calculating the surface excess of ionic surfactants at the air–solution interface in the presence of mixed counterions has been demonstrated.

The results of this study also envisage the possibilities of tuning the properties of ionic surfactant systems by mixing surfactants with different counterions, which may find application in the design of surfactant-containing formulations. A few mixed surfactants containing same hydrocarbon tail and two different counterions were studied [37–41], but such mixed systems with AOT-based surfactants have not been explored. The findings of this work may advance the field of study on mixed surfactants by opening up scope for determining (i) the pair of counterions that exhibit synergism in cmc and (ii) the dependence of this synergism due to mixed counterions on the nature of the hydrocarbon tail.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcis.2011.10.055.

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