Urea effect on aggregation and adsorption of sodium dioctylsulfosuccinate in water

2 AUTHORS:

Uttam Thapa
North Eastern Hill University
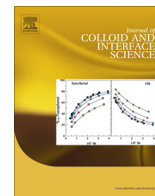8 PUBLICATIONS   36 CITATIONS

SEE PROFILE

Kochi Ismail
North Eastern Hill University
86 PUBLICATIONS   676 CITATIONS

SEE PROFILE

Urea effect on aggregation and adsorption of sodium dioctylsulfosuccinate in water

U. Thapa, K. Ismail *

Department of Chemistry, North-Eastern Hill University, Shillong 793 022, India

ARTICLE INFO

ABSTRACT

Understanding the mechanism that controls the folding/unfolding of proteins in the presence of urea continues to be a subject of research, and since micelles mimic biological aggregates, equal importance has been given to the study of surfactants in the presence of urea. Despite several studies on the effect of urea on the behavior of reverse micelles and microemulsions based on sodium dioctylsulfosuccinate (AOT), the urea effect on AOT regular micelles has not been investigated and hence it is studied herein by using surface tension, steady-state fluorescence, and dynamic light scattering methods. The effect of urea on the behavior of AOT is found to be different below and above 1.0 mol kg^{-1} urea (c_u). The critical micelle concentration (cmc) is almost independent of urea concentration below c_u, whereas it increases with increasing urea amount above c_u. In AOT + urea aqueous solution below c_u, added NaCl at a particular critical concentration (c^*) induces sudden increase in the values of (i) counterion binding constant, (ii) aggregation number, (iii) fluorescence intensity ratio of pyrene excimer to monomer, and (iv) hydrodynamic diameter of AOT aggregate, whereas such changes are suppressed by urea above c_u. NaCl-induced shape change in AOT micelle takes place if urea concentration is below c_u, but hindered above c_u. The adsorption behavior of AOT at the air–solution interface as a function of NaCl is also found to be different below and above c_u. The urea effect is explained in terms of increase in the polarity of the medium, better solvation of head groups and counterions, and weakening of head group–head group and head group–counterion interactions.

1. Introduction

Urea denatures proteins, enhances solubility of hydrocarbons in water, and inhibits aggregation of surfactants. Owing to these important properties of urea, extensive studies have been made using urea as an additive. Understanding the underlying mechanism that controls the folding/unfolding of proteins in the presence of urea continues to be a subject of research [1–8]. Generally, two mechanisms known as direct and indirect models are used to explain the effect of urea on protein. In the direct model, the denaturing effect of urea is attributed to direct interactions between urea and the protein, whereas in the indirect model, urea disrupts the water structure thereby weakening the hydrophobic effect and causing protein denaturation. Wallqvist et al. [9] have proposed another explanation for the denaturation of proteins by urea, which they called as outside-in action of urea. According to this explanation, urea molecules preferentially adsorb onto charged hydrophilic residues on the protein surface leading to repulsion between the residues, which gives rise to swelling of protein and

penetration of water into the protein core leading eventually to denaturation of protein.

Micelles mimic biological aggregates and hence equal importance has been given to the study of surfactants in the presence of urea. The effect of urea on surfactants indicates mainly increment in critical micelle concentration (cmc) and reduction in the counterion affinity toward micelles [10–21]. Attempts have been made to explain the urea effect on the solution and surface properties of surfactants in light of direct or indirect mechanism. Politi and coworkers [21] have proposed yet another explanation for the urea effect in which urea is considered to form more polar water with enhanced hydrophilicity resulting stronger solvation of polar or ionic head groups and a reduction in ion-pair formation. The chemical trapping method employed by Romsted et al. [19,20] showed that the interfacial concentration of urea is essentially the same as the bulk concentration indicating no preferential binding of urea to the micellar interface. According to this finding of Romsted et al. [19,20], the presence of urea at the interface weakens the headgroup–counterion interaction thereby attributing to the destabilization of micelle or increase in the cmc.

In addition to the general destabilizing effect of urea on protein and surfactants, there are also a few reports [22–24] on its stabilizing effect. It has been reported [22,23] that urea (or n-butylurea)

* Corresponding author. Address: Department of Chemistry, North-Eastern Hill University, NEHU Campus, Shillong 793 022, India. Fax: +91 364 2550486.
E-mail addresses: kismail@nehu.ac.in, kinehu@hotmail.com (K. Ismail).

decreases the cmc of sodium dodecylsulfate (SDS) in aqueous medium if the urea concentration is $\leqslant 0.25$ M (M = mol dm^{-3}) and the usual increase in cmc occurs only when the urea concentration exceeds 0.25 M. Similarly, urea decreases the cmc of sodium *N*-(11-acrylamidoundecanoyl)-L-valinate (SAUV), an amino acid surfactant, in the region where urea concentration is less than 1 M [24].

Urea has been reported [25–32] to have different types of effect on reverse micelles and microemulsions containing sodium dioctylsulfosuccinate (AOT). In AOT/CCl$_4$ and AOT/benzene reverse micelles with R_{urea} = 0.5 (R_{urea} is the molar ratio of urea to AOT), urea is encapsulated as molecular clusters and it interacts with AOT by undergoing hydrogen bonding between its amino groups and the sulfonate head group of AOT [25,26]. In these reverse micelles, the β-chain of AOT (chain containing sulfonate group) is closer to urea than the α-chain [25]. On the other hand, if R_{urea} < 0.13, urea is dispersed as monomers in the core of the AOT/CCl$_4$ reverse micelle [26]. In AOT/n-hexane/water microemulsion, urea induces percolation in conductivity with percolation threshold decreasing with increasing urea concentration and also produces a decrease in conductivity with increasing temperature when the urea concentration is 5 M and water volume fraction is in the range of 0.03–0.08, which is an anomalous behavior [27,29]. Moreover, preferential solubilization of urea at the interfacial region of the AOT/n-hexane/water microemulsion has been reported [27]. Binding of urea to the interface has also been reported in AOT/isooctane reverse micelles [30]. The dynamics of urea inside AOT/n-heptane reverse micelle is reported [31] to be much slower than that of water indicating presence of networked urea in the reverse micelle. Chakraborty et al. [32] reported an interesting stabilizing effect of urea at low concentration in AOT/n-heptane/water microemulsion. They observed that the value of the molar ratio of water to AOT (ω_{cr}) beyond which the micelles become unstable increased as the urea amount in the central pool increased if the urea concentration is below 1 M and decreased if the urea concentration is above 1 M [32].

Despite several studies on the effect of urea on the behavior of surfactants and AOT based reverse micelles and microemulsions, no report is surprisingly available to the best of our knowledge on the effect of urea on AOT regular micelles. AOT is a double-chained anionic surfactant with some special properties, e.g., it forms microemulsion without the presence of a cosurfactant [33–36] and it has a special counterion binding behavior (SCB) [37–39], viz. the value of its counterion binding constant (β) undergoes a sudden twofold increase in aqueous NaCl solution when NaCl concentration is about 0.015 mol kg^{-1}. The effect of urea on the aggregation behavior of AOT in water has a bearing on the effect that urea exhibits on AOT based reverse micelles and microemulsions. It is therefore necessary to have an understanding of the urea effect on the properties of AOT in aqueous medium. With this view in mind, we have investigated in this work the aggregation, adsorption, and the SCB of AOT in water + urea media using surface tension, fluorescence, and dynamic light scattering (DLS) methods.

2. Materials and methods

AOT (Sigma, 99%), pyrene (Fluka), cetylpyridinium chloride (CPC; Sigma), and NaCl (Merck, 99%) were used as received. The commercial sample of urea (Rankem, 99.5%) was recrystallized twice from its aqueous solution. Milli-Q grade water was used for preparing solutions.

Surface tension measurements were made by using Krüss K11 tensiometer and the Wilhelmy plate method. The fluorescence emission spectra of 4 µm pyrene (excitation wavelength was 335 nm) in the absence and presence of quencher (CPC) were recorded in a Hitachi F4500 FL spectrophotometer. A Haake DC10 circulation bath was used for maintaining the temperature at 25 °C during surface tension and fluorescence measurements.

Dynamic light scattering (DLS) measurements were made with a Malvern Zetasizer Nano ZS instrument operating at 633 nm (4 mW HeNe laser is used) and 90° scattering angle. Samples were filtered through a 0.22 µm membrane filter prior to measurements. The scattering intensity data were processed using the instrumental software to obtain the hydrodynamic diameter (d_H) and the size distribution of aggregates in each sample. During DLS measurements, the temperature was maintained at 25 °C by the built-in temperature control unit (Peltier) of the instrument.

3. Results and discussion

3.1. Critical micelle concentration

The surface tension (γ) of aqueous urea solutions is found to be slightly more than that of water (Fig. 1A) which is in agreement with the reported trend [40,41]. Experimental surface tension values of aqueous AOT solution containing different amounts of urea are shown in Fig. 1B, and the cmc values of AOT determined from these surface tension isotherms are represented in Fig. 2.

The cmc values of AOT in aqueous urea solutions were also determined by measuring the intensity ratio I_1/I_3 of pyrene fluorescence emission. I_1 and I_3 refer to the emission intensities of pyrene at 373 and 384 nm, respectively. The plot of I_1/I_3 versus concentration of AOT is shown in Fig. 3. Once micelles are formed, solubilization of pyrene in the micellar phase takes place and the polarity of pyrene environment changes causing decrease in the value of I_1/I_3. The cmc values chosen from Fig. 3 as the concentrations of AOT at which sharp decrease in the value of I_1/I_3 begins were found to be lower (to a maximum extent of 0.6 mmol kg^{-1}) than those determined from the surface tension data. Aguair et al. [42] suggested an analytical method for determining cmc from the I_1/I_3 data. In this method, I_1/I_3 data are fitted to the sigmoid type equation of the form

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

In Eq. (1), c represents the surfactant concentration, x_0 is the value of c corresponding to the center of the sigmoid, A_1 and A_2 are the upper and lower limits of the sigmoid, respectively, and the term b reflects the range of c wherein sudden change in I_1/I_3 occurs. The cmc values taken as equal to x_0 are shown in Fig. 2, and they are higher (to a maximum extent of 0.8 mmol kg^{-1}) than those
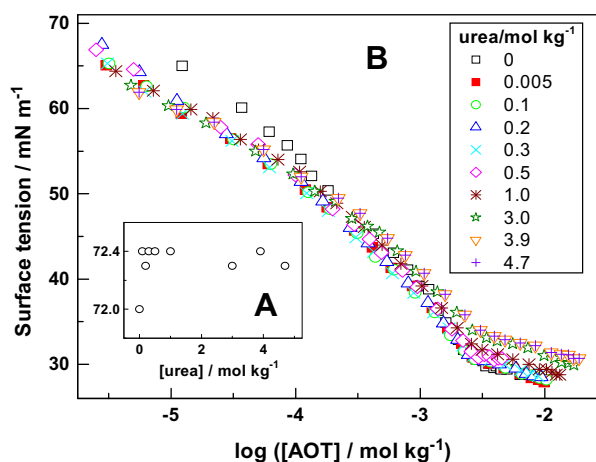

Fig. 1. Surface tension values of aqueous urea solutions (A) and aqueous AOT solutions in the presence of urea (B).
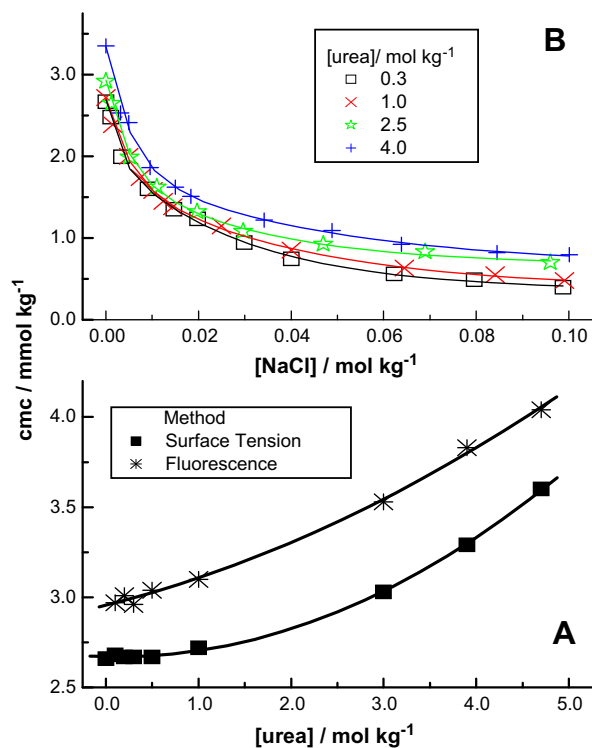
Fig. 2. Variation of cmc of AOT in aqueous medium (A) with urea concentration in the absence of NaCl and (B) with NaCl concentration at fixed urea concentrations.
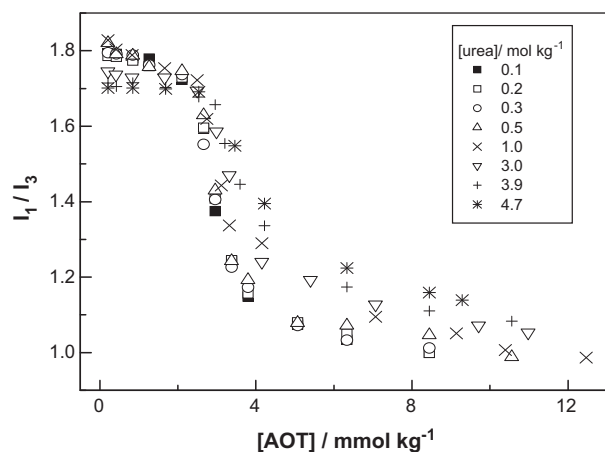

Fig. 3. Variation of I_1/I_3 of pyrene with AOT concentration at different urea concentrations.

determined from the surface tension data. Reported studies [42,43] have revealed that correlation between cmc and x_0 (cmc = x_0 or cmc < x_0 or cmc > x_0) depends upon the type of surfactant and the solvent. However, the cmc determined from surface tension and fluorescence methods (cmc = x_0) varies with urea concentration in a similar fashion (Fig. 2A).

According to Dias et al. [21], water becomes more polar by adding urea and the urea–water mixture solvates polar and ionic groups better than water alone. Romsted et al. [19,20] reported that the interfacial concentration of urea is essentially the same as that in the bulk solution. The presence of urea at the micelle-solution interface weakens the repulsive interaction between the head groups owing to increase in dielectric constant and better screening of the head groups due to larger size of urea molecules

(about 2.5 times more than the size of water [24]) that solvate the head groups. This type of influence by urea will have a stabilizing effect on aggregation of surfactant and the cmc will decrease. Such a stabilizing effect of urea is reported to be responsible for the decrease in cmc of SDS and SAUV by the addition of urea in the low urea concentration region [23,24]. On the other hand, better solvation of counterions and head groups will screen them better, which along with increased dielectric constant will weaken the head group–counterion interaction at the micelle–solution interface. This actually induces destabilizing effect and cause increase in cmc. Stronger solvation of polar groups in the presence of urea instead of the direct or indirect mechanism has been illustrated as responsible for the destabilizing effect of urea by the reported studies [17,18,21] on different surfactants. Urea can thus induce both stabilizing and destabilizing effects on an ionic surfactant and the relative strength of these two effects will depend upon the concentration range of urea and the nature of surfactant. In the case of AOT, it may be noted from Fig. 2A that cmc begins to increase from about 0.8 mol kg^{-1} urea. However, the increase in cmc in the region of 0 to 1.0 mol kg^{-1} urea was estimated to be about 2% only per mole of urea, whereas that in the region of 1.0 to 4.7 mol kg^{-1}, urea was found to be about 9% per mole of urea. Therefore, we considered 1.0 mol kg^{-1} as the critical urea concentration, c_u. Up to c_u, the stabilizing and destabilizing effects of urea on the cmc of AOT appear to compensate each other thereby resulting in almost no change in cmc. Above c_u, the destabilizing effect appears to dominate and hence cmc increases with increase in urea amount.

3.2. Counterion binding

In order to estimate the counterion binding constant (β) of AOT, cmc values of AOT were determined as a function of NaCl concentration at fixed urea concentrations by surface tension method and these cmc values are presented in Fig. 2B. With increasing concentration of NaCl, the cmc decreases which is a normal trend for all ionic surfactants in all media and is attributed to the reduction in the repulsive interaction between the head groups due to added counterions. The value of β was determined from the Corrin–Harkins (CH) equation:

$$\ln \text{cmc} = A - \beta \ln(\text{cmc} + c_e) \qquad (2)$$

where c_e represents concentration of added NaCl and A is a constant related to the standard free energy of micellization. The CH plots are shown in Fig. 4. The values of cmc of AOT in water ([urea] = 0) as a
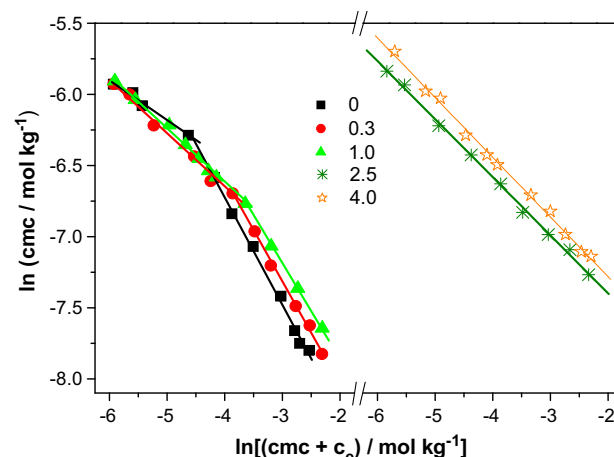

Fig. 4. CH plots of AOT in water + urea media. Urea concentrations in mol kg^{-1} are indicated in the inset.

function of NaCl concentration were taken from our earlier work [37]. The values of β for AOT at four different urea concentrations are given in Table 1. Fig. 4 clearly shows that AOT has two values of β in solutions containing 0.3 and 1.0 mol kg^{-1} urea similar to that in water [37]. In this concentration range of urea, i.e., between 0 and 1.0 mol kg^{-1}, as the concentration of urea increased, (i) the lower value of β remained almost constant, (ii) the higher value of β decreased, and (iii) the critical concentration of NaCl (c^*) at which the value of β switches over from lower to higher value increased slightly (Table 1). The decrease in higher value of β by the addition of urea is in accordance with the reported [10,12,13] decreasing trend of β of different ionic surfactants with increasing amount of urea in water. In aqueous media containing 2.5 and 4 mol kg^{-1} of urea, AOT has only one value of β equal to the lower value of β in water (Table 1). In other words, higher concentrations of urea (above 1.0 mol kg^{-1}) destroy the SCB of AOT. From Fig. 4, it may be seen that the SCB of AOT ceases when the urea concentration lies between 1.0 and 2.5 mol kg^{-1}. We however considered 1.0 mol kg^{-1} as the critical urea concentration above which the SCB of AOT disappears in view of the c_u value adopted on the basis of cmc variation with urea concentration as discussed above. It has been reported [39] that at c^*, the AOT micelle undergoes a shape change (prolate spheroid to rod-like) and hence an increase in the value of c^* by the addition of urea indicates that urea hinders the shape change in AOT micelle. Therefore, added urea has a tendency to suppress the NaCl-induced shape change in AOT micelle leading to no shape change when the urea concentration exceeds 1.0 mol kg^{-1}. The property of urea to hinder shape transition of SDS micelle is already known [14,20,44,45].

In the region where urea concentration is $\leqslant$1.0 mol kg^{-1}, the counterion binding behavior of AOT micelle is similar to that in water with no urea because the stabilizing and destabilizing effects of urea balance each other as mentioned above. When urea concentration is greater than 1.0 mol kg^{-1}, the destabilizing effect of urea predominates, and as a result, excessive counterion binding is hindered due to which β does not take the higher value.

3.3. Miceller size and shape change

3.3.1. Steady-state fluorescence quenching (SSFQ) study

The aggregation number, N_{agg}, of AOT as a function of NaCl concentration in water + urea media was determined from the fluorescence quenching data of pyrene by using the equation:

$$\ln(I_0/I_q) = [Q]N_{agg}(c - cmc) \qquad (3)$$

where I_0 and I_q represent intensities of fluorescence emission of pyrene in the absence and presence of the quencher CPC, respectively. [Q] refers to the quencher concentration. The value of $c - cmc$ was kept constant at 0.002 mol kg^{-1}. In aqueous AOT solutions containing 0.3 and 1.0 mol kg^{-1} urea, as in the case of β, a sudden increase in N_{agg} is observed near c^* similar to the trend observed in water (Fig. 5A). On the other hand, in solutions containing 2.5 and 4.0 mol kg^{-1} urea, only a gradual increase in N_{agg} was noticed
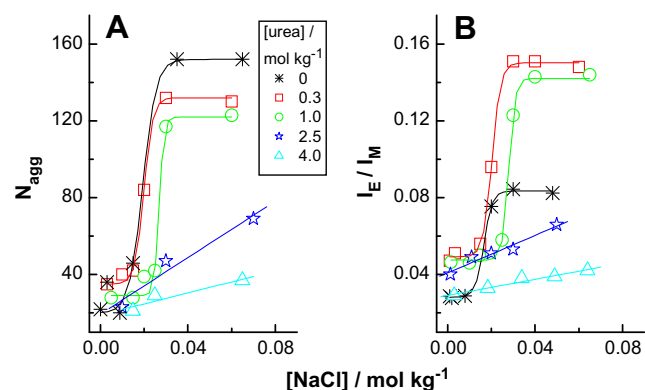

Fig. 5. Variation of aggregation number of AOT (A) and I_E/I_M of pyrene (B) with NaCl concentration in water + urea solution.

(Fig. 5A). Thus, a sudden increase (by a factor of ~3) in the aggregation number of AOT can be induced by adding NaCl if the urea amount is less than or equal to the critical amount of 1.0 mol kg^{-1} and it is not possible when the urea content exceeds this critical amount. Failure of NaCl to induce sudden increase in aggregation number when urea concentration is greater than 1.0 mol kg^{-1} is attributable to the destabilizing effect of urea.

An attempt has been made to verify whether AOT micelle undergoes shape change at c^*. It has been reported that the pyrene I_E/I_M ratio can detect the NaCl induced sphere to rod transition of SDS micelles as its value increases sharply near the critical concentration of NaCl where SDS micelle undergoes shape change from spherical to rod-like [46]. Here, I_E and I_M are the intensities of the fluorescence emission of the pyrene excimer and monomer, respectively. We determined the values of I_E/I_M from the fluorescence emission spectra of pyrene in water + AOT and water + AOT + urea media recorded as a function of NaCl concentration. Representative emission spectra of pyrene in water + 1.0 mol kg^{-1} urea + AOT + NaCl solution are shown in Fig. 6. In the present study, I_E is measured at 467 nm and I_M at 384 nm. The variation of I_E/I_M with NaCl concentration is shown in Fig. 5B. From Fig. 5B, it is quite clear that in water + AOT + NaCl medium, the value of
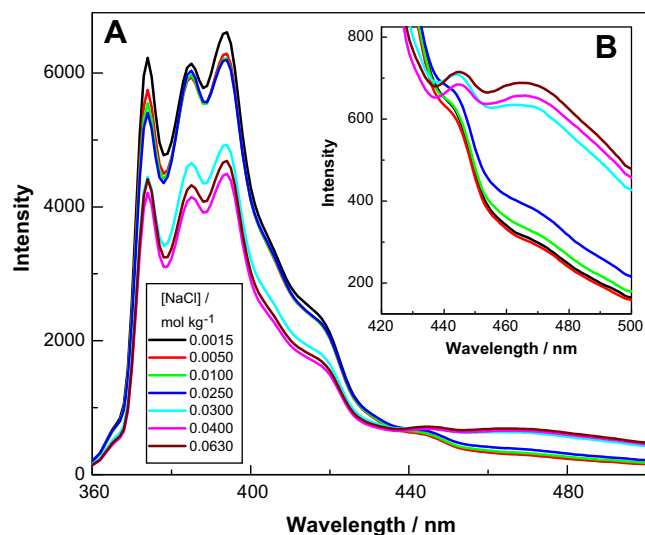
Table 1
Counterion binding constant (β) values of AOT in urea–water media at 25 °C. (c^* is the concentration of NaCl at which changeover in the value of β occurs).

[Urea] (mol kg^{-1})	c^* (mol kg^{-1})	β	
		[NaCl] $\leqslant c^*$	[NaCl] > c^*
0	0.015	0.39	0.82
0.3	0.020	0.39	0.71
1.0	0.025	0.39	0.64
2.5	–	0.41	–
4.0	–	0.42	–

Fig. 6. Fluorescence emission spectra of pyrene in water + 1.0 mol kg^{-1} urea + AOT ($c - cmc = 0.002$ mol kg^{-1}) + NaCl media. Concentrations of NaCl in mol kg^{-1} are indicated in the inset. The emission bands of the pyrene excimer are displayed more clearly in the layer B.

the ratio I_E/I_M increases suddenly near c^* and therefore a sudden shift in the value of I_E/I_M can be used as an indication of the micellar shape change since in water shape change in AOT micelle at c^* has been confirmed earlier by the small-angle neutron scattering (SANS) measurement [39]. It is evident from Fig. 5B that at c^* shape change in AOT micelle takes place in the presence of 0.3 and 1.0 mol kg^{-1} urea, but more urea (in the present study 2.5 and 4.0 mol kg^{-1}) than the critical value (1.0 mol kg^{-1}) stops the shape change in AOT micelle. These are in complete agreement with the inferences made from the CH plots and aggregation number. When the urea amount at the micelle–solution interface exceeds the critical amount of 1.0 mol kg^{-1}, the destabilizing effect becomes predominant enough to hinder both sharp increase in aggregation number and change in micellar shape.

3.3.2. DLS study

Although dynamic light scattering technique provides a useful method to measure the size and polydispersity of aggregates, DLS measurements on aqueous AOT solution are known to give very intriguing results. Reported values of d_H of AOT aggregates determined from DLS study [47–49] are abnormally larger than the values expected from the aggregation numbers of AOT measured by the SSFQ and SANS methods [37,39,50]. The measured value of d_H in aqueous solution of 0.015 mol kg^{-1} AOT is found to be 157 nm which is in good agreement with the reported values [47–49]. Such large size AOT aggregates are considered to be predominantly vesicles. However, the nature of these aggregates is yet to be understood fully, particularly in view of the fact that the volume of AOT aggregate we get from DLS study is about 10^5 times larger than that estimated from the aggregation number ($\sim$35) determined by using the SSFQ and SANS methods (the bare volume of monomer tail and head group of AOT is taken as 611 Å^3) [37,39,50]. Nevertheless, the dependence of d_H of AOT aggregates on NaCl concentration in the presence of urea is noteworthy which is shown in Fig. 7. On adding NaCl, the value of d_H increases sharply and attains maximum near c^* or increases suddenly near c^* to a maximum without much increase initially when the solution contains 0.3 mol kg^{-1} or 1.0 mol kg^{-1} urea, respectively, whereas no such type of sharp/sudden changes takes place in d_H when the urea amount in solution is 2.5 or 4.0 mol kg^{-1} (Fig. 7). This is in agreement with the trend in the variation of N_{agg} observed on adding NaCl to AOT solutions containing 0.3, 1.0, 2.5, and 4.0 mol kg^{-1} urea (Fig. 5A). Thus, in spite of DLS and fluorescence results indicating discrepancy in the size and shape (vesicle or micelle) of
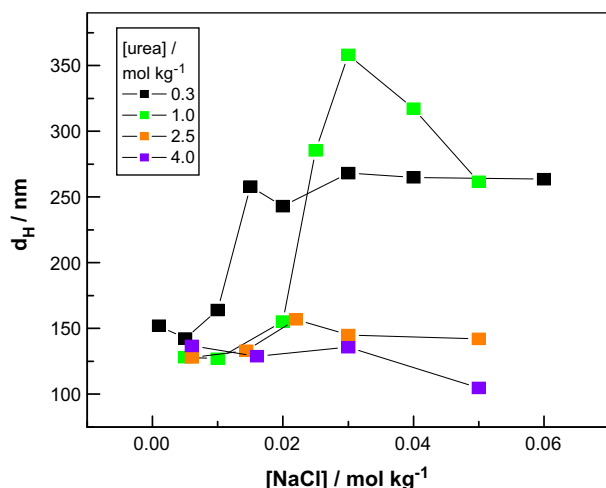
AOT aggregates, DLS measurements also confirm that urea can retain or suppress completely the ability of added NaCl to produce sudden change in the size of AOT aggregates near c^* depending upon whether the urea concentration is less or more than the critical value c_u, respectively.

3.4. Adsorption

Surface excess of AOT at the cmc (Γ_{cmc}) as a function of NaCl concentration was calculated by using the expression

$$\Gamma_{cmc} = -\left(\frac{1}{RT}\right)\left(\frac{1}{1 + \frac{cmc}{cmc + c_e}}\right)\left(\frac{d\gamma}{d\ln c}\right) \qquad (4)$$

In Eq. (4), R and T represent gas constant and absolute temperature, respectively. The value of the slope $d\gamma/d\ln c$ at the cmc was determined from the surface tension isotherm (Fig. 1). In the absence of NaCl, Eq. (4) reduces to the form $\Gamma_{cmc} = -(1/(2RT))(d\gamma/d\ln c)$ and Γ_{cmc} calculated using this expression varied from 1.63 to 1.24 µmol m^{-2} while the surface area per AOT molecule ($A_0 = 1/[N_A \cdot \Gamma_{cmc}]$, where N_A refers to the Avogadro number) varied from 1.02 to 1.33 nm^2 when the urea concentration changed from 0 to 4.7 mol kg^{-1} (Fig. 8A). Such dependence of Γ_{cmc} or A_0 on urea concentration may be understood in light of the following two facts: (i) on adding urea, the water molecules around the hydrocarbon tails are replaced by urea, which causes decrease in hydrophobicity of AOT and increase in the solubility of AOT in water + urea media. This will reduce the adsorption of AOT at the air–solution interface and accordingly Γ_{cmc} decreases by adding urea. (ii) Firstly, urea increases the dielectric constant of the subphase below the air–solution interface as it does in the bulk phase because the concentration of urea at the interface is almost same as in the bulk as reported by Romsted et al. [19,20]. This weakens the head group–counterion
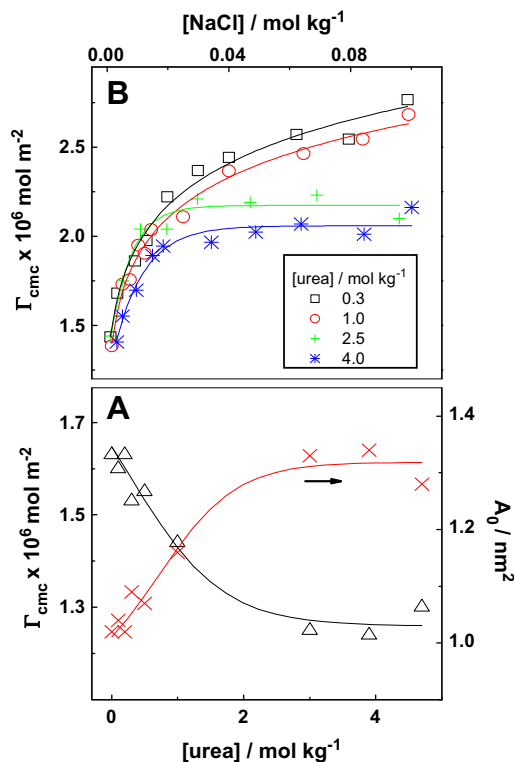

Fig. 7. Variation of hydrodynamic diameter of AOT aggregates with NaCl concentration in water + urea media.

Fig. 8. Variation of surface excess of AOT with (A) urea concentration in the absence of NaCl and (B) NaCl concentration in the presence of urea (concentration shown in the inset).

interaction. Secondly, better solvation of head groups and counterions due to added urea [21] also weakens the head group–counterion interaction (steric effect). As a result, the extent of counterion binding to the head groups near the air–solution interface reduces causing the repulsive interaction between the negatively charged head groups to increase. Such increase in the repulsive interaction stretches the head groups at the interface thereby increasing the A_0 value or decreasing the Γ_{cmc} value (Fig. 8A). On adding NaCl at a fixed urea concentration, the counterion concentration at the air–solution interface increases and this decreases the repulsive interaction between the head groups. Therefore, addition of NaCl decreases A_0 or increases Γ_{cmc} (Fig. 8B). Once again, it is found from Fig. 8B that the dependence of Γ_{cmc} on NaCl concentration when [NaCl] > 0.02 mol kg^{-1} (i.e., above c^*) is different below and above 1.0 mol kg^{-1} urea concentration.

4. Conclusions

In view of the results of the present and reported [21–24] studies, it has become clear that urea has both stabilizing and destabilizing effects on the aggregation behavior of surfactants. The nature of surfactant and the concentration of urea determine which effect out of the two dominates. For example, in the case of SDS, the stabilizing effect prevails if the urea concentration is ⩽0.25 M and the destabilizing effect predominates above 0.25 M urea [23]. Similarly, in the case of SAUV surfactant, urea exhibits stabilizing effect below 1 M urea and destabilizing effect above 1 M urea [24]. On the other hand, in AOT solution, as noticed in this study, the urea effect is negligible below 1.0 mol kg^{-1} urea due to balancing of the two effects and the moment urea concentration exceeds 1.0 mol kg^{-1} the destabilizing effect predominates. Without applying the direct or indirect mechanism, the stabilizing and destabilizing effects of urea are explained by taking into account (i) water becoming more polar in the presence of urea, (ii) better solvation of polar and ionic groups in water–urea mixture [21], and (iii) almost same urea concentration at the interface and bulk [19,20]. In the presence of urea, weakening of head group–head group and head group–counterion interactions at the interface is essentially responsible for the stabilizing and destabilizing effects of urea, respectively.

This study has ascertained the stabilizing and destabilizing effects of urea and out of the two which effect dominates is dictated by the nature of the surfactant and the amount of urea.

Acknowledgments

References

[1] X. Chen, L.B. Sagle, P.S. Cremer, J. Am. Chem. Soc. 129 (2007) 15104.
[2] L.B. Sagle, Y. Zhang, V.A. Litosh, X. Chen, Y. Cho, P.S. Cremer, J. Am. Chem. Soc. 131 (2009) 9304.
[3] R. Zangi, R. Zhou, B.J. Berne, J. Am. Chem. Soc. 131 (2009) 1535.
[4] A.K. Hüsecken, F. Evers, C. Czeslik, M. Tolan, Langmuir 26 (2010) 13429.
[5] M.G. Ortore, R. Sinibaldi, F. Spinozzi, F. Carsughi, D. Clemens, A. Bonincontro, P. Mariani, J. Phys. Chem. B 112 (2008) 12881.
[6] M.C. Stumpe, H. Grubmüller, PLoS Comput. Biol. 4 (2008) e1000221 (pp. 1–10).
[7] S. Chodankar, V.K. Aswal, J. Kohlbrecher, R. Vavrin, A.G. Wagh, Pramana 71 (2008) 1021.
[8] Z. Yang, P. Xiu, B. Shi, L. Hua, R. Zhou, J. Phys. Chem. B 116 (2012) 8856.
[9] A. Wallqvist, D.G. Covell, D. Thirumalai, J. Am. Chem. Soc. 120 (1998) 427.
[10] P.K. Das Gupta, S.P. Moulik, Colloid Polym. Sci. 267 (1989) 246.
[11] N. Sarkar, K. Bhattacharyya, Chem. Phys. Lett. 180 (1991) 283.
[12] P. Baglioni, L. Dei, E. Ferroni, L. Kevan, Colloid Polym. Sci. 84 (1990) 55.
[13] S. Causi, R.D. Lisi, S. Milioto, N. Tirone, J. Phys. Chem. 95 (1991) 5664.
[14] G. Briganti, S. Puvvada, D. Blankschtein, J. Phys. Chem. 95 (1991) 8989.
[15] F.H. Florenzano, L.G.C.D. Santos, I.M. Cuccovia, M.V. Scarpa, H. Chaimovich, M.J. Politi, Langmuir 12 (1996) 1166.
[16] O. Greksakova, J. Oremusova, Tenside Surf. Det. 39 (2002) 40.
[17] H. Raghuraman, S.K. Pradhan, A. Chattopadhyay, J. Phys. Chem. B 108 (2004) 2489.
[18] J.M. Hierrezuelo, J.A. Molina-Bolivar, C.C. Ruiz, J. Phys. Chem. B 113 (2009) 7178.
[19] L.S. Romsted, J. Zhang, I.M. Cuccovia, M.J. Politi, H. Chaimovich, Langmuir 19 (2003) 9179.
[20] L.S. Romsted, Langmuir 23 (2007) 414.
[21] L.G. Dias, F.H. Florenzano, W.F. Reed, M.S. Bapista, S.M.B. Souza, E.B. Alvarez, H. Chaimovich, I.M. Cuccovia, C.L.C. Amaral, C.R. Brasil, L.S. Romsted, M.J. Politi, Langmuir 18 (2002) 319.
[22] M. Abu-Hamdiyyah, L. Al-Mansour, J. Phys. Chem. 83 (1979) 2236.
[23] S. Kumar, N. Parveen, Kabir-ud-Din, J. Phys. Chem. B 108 (2004) 9588.
[24] S. Roy, J. Dey, J. Colloid Interface Sci. 290 (2005) 526.
[25] L. Ceraulo, E. Dormond, A. Mele, V.T. Liveri, Colloid Surf. A 218 (2003) 255.
[26] G. Calvaruso, A. Minore, V.T. Liveri, J. Colloid Interface Sci. 243 (2001) 227.
[27] C.L.C. Amaral, O. Brino, H. Chaimovich, M.J. Politi, Langmuir 8 (1992) 2417.
[28] C.L.C. Amaral, R. Itri, M.J. Politi, Langmuir 12 (1996) 4638.
[29] R. Itri, C.L.C. Amaral, M.J. Politi, J. Chem. Phys. 111 (1999) 7668.
[30] F.C.L. de Almeida, H. Chaimovich, S. Schreier, Langmuir 10 (1994) 1786.
[31] A. Sengupta, R.V. Khade, P. Hazra, J. Phys. Chem. A 115 (2011) 10398.
[32] A. Chakraborty, M. Sarkar, S. Basak, J. Colloid Interface Sci. 287 (2005) 312.
[33] S. Nave, J. Eastoe, Langmuir 16 (2000) 8733.
[34] S. Nave, J. Eastoe, Langmuir 16 (2000) 8741.
[35] S. Nave, J. Eastoe, R.K. Heenan, D. Steytler, I. Grillo, Langmuir 18 (2002) 1505.
[36] S. Nave, A. Paul, J. Eastoe, A.R. Pitt, R.K. Heenan, Langmuir 21 (2005) 10021.
[37] I.M. Umlong, K. Ismail, J. Colloid Interface Sci. 291 (2005) 529.
[38] I.M. Umlong, J. Dey, S. Chanda, K. Ismail, Bull. Chem. Soc. Jpn. 80 (2007) 1522.
[39] J. Dey, J. Bhattacharjee, P.A. Hassan, V.K. Aswal, S. Das, K. Ismail, Langmuir 26 (2010) 15802.
[40] K. Tajima, M. Iwahashi, Bull. Chem. Soc. Jpn. 46 (1973) 3370.
[41] R. Breslow, T. Guo, Proc. Natl. Acad. Sci. USA 87 (1990) 167.
[42] J. Aguiar, P. Carpena, J.A. Molina-Bolívar, C.C. Ruiz, J. Colloid Interface Sci. 258 (2003) 116.
[43] D. Das, K. Ismail, J. Colloid Interface Sci. 327 (2008) 198.
[44] S. Kumar, D. Sharma, G. Ghosh, Kabir-ud-Din, Colloid Surf. A 264 (2005) 203.
[45] N. Gull, S. Kumar, B. Ahmad, R.H. Khan, Kabir-ud-Din, Colloid Surf. B 51 (2006) 10.
[46] A. Chaudhuri, S. Haldar, A. Chattopadhyay, Biochem. Biophys. Res. Commun. 390 (2009) 728.
[47] Y. Fan, Y. Li, G. Yuan, Y. Wang, J. Wang, C.C. Han, H. Yan, Langmuir 21 (2005) 3814.
[48] M.M. Velazquez, M. Valero, F. Ortega, J.B. Rodriguez-Gonzalez, J. Colloid Interface Sci. 316 (2007) 762.
[49] R. Saha, P.K. Verma, R.K. Mitra, S.K. Pal, Colloids Surf. B 88 (2011) 345.
[50] E.Y. Sheu, S.H. Chen, J.S. Huang, J. Phys. Chem. 91 (1987) 3306.