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ORIGINAL CONTRIBUTION

Effect of size of tetraalkylammonium counterions on the temperature dependent micellization of AOT in aqueous medium

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Abstract Different tetraalkylammonium, viz. $N^+(CH_3)_4$, $N^+(C_2H_5)_4$, $N^+(C_3H_7)_4$, $N^+(C_4H_9)_4$ along with simple ammonium salts of bis (2-ethylhexyl) sulfosuccinic acid have been prepared by ion-exchange technique. The critical micelle concentration of surfactants with varied counterions have been determined by measuring surface tension and conductivity within the temperature range 283–313 K. Counterion ionization constant, α, and thermodynamic parameters for micellization process viz., ΔG_m^0, ΔH_m^0, and ΔS_m^0 and also the surface parameters, Γ_{max} and A_{min}, in aqueous solution have been determined. Large negative ΔG_m^0 of micellization for all the above counterions supports the spontaneity of micellization. The value of standard free energy, ΔG_m^0, for different counterions followed the order $N^+(CH_3)_4 > NH_4^+ > Na^+ > N^+(C_2H_5)_4 > N^+(C_3H_7)_4 > N^+(C_4H_9)_4$, at a given temperature. This result can be well explained in terms of bulkiness and nature of hydration of the counterion together with hydrophobic and electrostatic interactions.

Keywords Aerosol-OT · Critical micelle concentration · Counterion · Thermodynamic parameters

Introduction

The colligative properties of surfactants do not vary in a simple way with concentration due to self assembly of amphiphiles forming micelles or vesicles [1]. The formation of an ionic micelle from monomeric ions results a balance between hydrophobic interactions between the hydrophobic part of the micelle-forming ions, electrostatic interactions between their hydrophilic charged parts, as well as with and between the counterions. In addition, the changes in hydration energies and specific interactions with counterions may also be important [2–6]. The strength and importance of these various interactions depend upon externally controllable factors, such as temperature and ionic strength on the properties of the particular ions involved. Moreover, the structure of the resulting micelle, in particular, its aggregation number, *n,* its shape, and the compactness of its electrical double layer show some kind of dependency [5]. Even the molecular conformation of some dimeric surfactants (known as Gemini surfactants) affects the micellization to a large extent [6]. Obviously, the actually existing micelles correspond to the lowest free-energy state of the system. Thus, the knowledge of critical micelle concentration (cmc) and thermodynamic quantities of micellization like Gibbs free energy ΔG_m^0, the enthalpy ΔH_m^0, or the entropy ΔS_m^0 at various temperatures have utmost importance from the view point of formation and stability of micelles.

A survey of phase diagram of ionic surfactants, in aqueous and in the presence of a cosolvent such as a long-chain alcohol, has demonstrated clearly that the valency of the counterion plays an important role in determining phase stability as well as the aggregation shape [7, 8]. It was shown that the swelling tendency of a lamellar interface is reduced considerably with a divalent counterion as com-

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pared to a monovalent one, which was explained in terms of a more extensive binding of the divalent counterions to the polar head groups of the surfactant lamellae. A substantial amount of work has already been carried out on the binding of monovalent counterions to micelle [4, 9, 10] for single tail anionic surfactant like dodecyl sulfate. The study of the effect of counterions eliminates some of the complications by leaving the properties of the amphiphilic ion as a constant factor and, thus, simplifies some of the interpretation of the experimental results. But, it often leads to complications connected with limited stability and preparative difficulties of the surfactant containing different counterions. Compared to cationic surfactants, the counterionic effect in micellization is less dramatic in anionic surfactants. However, when compared with Na^+ counterions, polyvalent ions usually markedly reduces the cmc [11] by several order of magnitude and lead the formation of large micelles that may be confirmed from the increase in micellar aggregation number [10, 12]. In aqueous solution, the micelles are known to be charged due to a fraction, α, of their counterion dissociates into the aqueous pseudophase. The value of α for a given pure surfactant is important because both the physical [13, 14] and chemical [15] properties of the micelle are influenced by surface charges.

Aerosol-OT (AOT, Sodium bis-(2-ethyl-1-hexyl) sulfosuccinate), having two hydrophobic tails, is an important anionic surfactant in the field of surface chemistry as well as in industry due to its rich phase behavior and the ability to form microemulsion [16]. This work is a part of a program to study the cmc and thermodynamic parameters of bis-(2-ethyl-1-hexyl) sulfosuccinate micelle within a wide range of temperature as the counterion is systematically made more bulky and hydrophobic. There are some evidences [4–6, 10] that the counterions exhibit mainly electrostatic interaction or, no chemical interaction is to be expected on the structural grounds. Therefore, it is the system where the cmc differences are rather small and the effect of ionic size and of physical adsorption can be best investigated. Thus, we investigate a series of tetraalkylammonium ion, such as $N^+(CH_3)_4$, $N^+(C_2H_5)_4$, $N^+(C_3H_7)_4$, $N^+(C_4H_9)_4$ along with NH_4^+ and Na^+. It should be mentioned that the cmc and thermodynamic parameters of the AOT having different tetraalkylammonium counterion have not yet been reported in the literature. Hence, our experimental goal is to determine the cmc of AOT with different counterions within the temperature range of 283–313 K and to determine the associated thermodynamic parameters of micellization, such as changes in standard Gibbs free energy (ΔG_m^0), standard enthalpy (ΔH_m^0), standard entropy (ΔS_m^0), maximum surface excess concentration (Γ_{max}), and the minimum areas per molecule (A_{min}) at the surface in order to examine the effect of counterionic sizes on the micellization.

Experimental section

Materials

Surfactants with the desired counterions were prepared by following the technique of Eastoe et al. [17] and the extended work of Temsamani et al. [4, 18]. A high-grade purified sample of AOT (>99% from Fluka, Switzerland) was converted into the surfactants bearing different counterions by ion-exchange technique using a strong ion exchange resin (Amberlite IR-120, 20–50 mesh, Loba Cheme, India). The process is described below:

A 10-g sample of AOT was dissolved in 20 mL of a 1:1 (*v*/*v*) mixture of water and ethanol. The solution was passed through a column (40 cm × 2 cm^2) of a strong ion exchanger in the H^+ form slowly. The resin was put in the acid form by using a large excess of a 0.20 M aqueous hydrochloric acid solution and washed with water until the complete removal of the excess acid takes place. The free sulfonic acid formed on passing the AOT (Na^+ salt) through the resin was, then, immediately neutralized with an aqueous solution of the hydroxides of the desired counterions (viz. NH_4^+, $N^+(CH_3)_4$, $N^+(C_2H_5)_4$, $N^+(C_3H_7)_4$, $N^+(C_4H_9)_4$). All the hydroxides of high purity were procured from Across Chem., Belgium. The solvent water was then removed fast by freeze drying and then keeping under vacuum (bath temperature 313 K) for several days, and the waxy solid was finally dried in vacuum over P_2O_5. These materials contain residual water, which were finally removed by the action of P_2O_5 (from Loba Cheme, India) on a solution of surfactant in isooctane (≥ 99.5% from Merck, India). The extent of Na^+/H^+ ion exchange was optimized by controlling the flow rate of the solution; finally, H^+ content of the AOT solution (acid form) was measured by titrating with standard NaOH. The extent of exchange was found to be more than 99%. Among all the ion-exchanged surfactants, tetrabutylammonium-AOT did not crystallize at room temperature even after keeping at low temperature for several months. It appeared as a highly viscous, colorless, semi-solid material. Doubly distilled water having conductivity of 2 $\mu S\ cm^{-1}$ was used throughout experiment.

Methods

The cmc values were determined from the surface tension as well as specific conductance data. It is customary to plot the (1) surface tension γ against the logarithmic value of the surfactant concentration C and the (2) conductance Λ against the concentration of the surfactant, where the break indicates the cmc of a particular system. The surface tension experiments were done by platinum ring detachment method using a Tensiometer (K9,

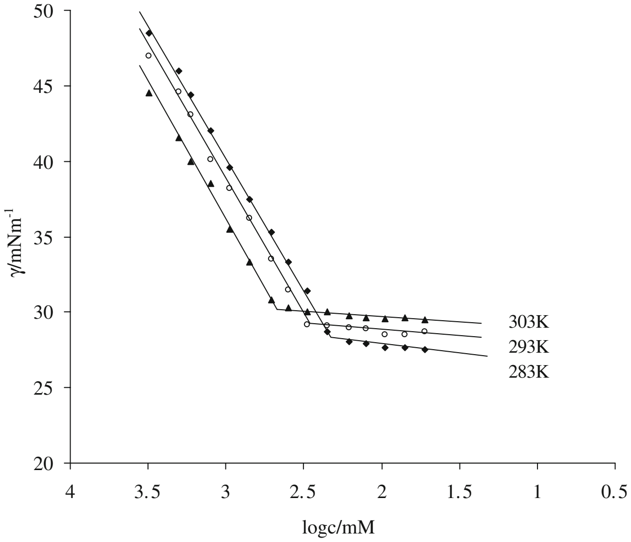

Fig. 1 Surface tension, γ, of AOT (Tetramethylammonium salt) in aqueous solution as a function of the logarithm of the surfactant concentration at 283, 293, and 303 K

KRŰSS; Germany) at different temperatures. The accuracy of the measurement was within ±0.1 m Nm^{-1}. Temperature of the system was maintained by circulating auto-thermostated water through a double-wall glass vessel containing the solution. Similar studies were also done conductometrically by using an electrical conductivity bridge (METTLER TOLEDO, Switzerland). The conductance values were uncertain within the limit of ±1%. Each measurement was repeated several times at each temperature in the ranges 283–313 K. Measurements were made at 5 K intervals of temperatures.

Results and discussion

Critical micelle concentration

The cmc corresponds to a concentration at which a very small but, often, clearly detectable concentration of the micelles exists. Typical experimental curves of salt-free systems are obtained in both surface tension and conductance measurements, and the cmc values determined for surfactant with each counterion are in close agreement with one another. The cmc of Na-AOT is also in good agreement with the literature value [19, 38]. The sharpness of the “break-point” is an indication of the purity of the surfactant used. Figures 1 and 2 are the representative plots obtained in the surface tension and conductivity measurements. Further results of surface tension experiments are presented in Table 1.

A critical examination of Table 1 shows that in all instances, the change of cmc with temperature is small. However, at a particular temperature, cmc depends upon the nature of the counterion following the order $N^+(CH_3)_4 > NH_4^+ > Na^+ > N^+(C_2H_5)_4 > N^+(C_3H_7)_4 > N^+(C_4H_9)_4$ (at temperature range <298 K). It seems that the hydrodynamic size of the counterion plays an important role along with the hydrophobicity of tetraalkylammonium ions. Measurement of partial molar volumes [20, 21] and calculation of hydration of micelles [22] by previous workers indicated that there was little loss of hydration water for this system during micellization. Therefore, the tightly bound hydration shell would limit the distance of closest approach. It is well known that the increase of the number of carbon atoms of hydrocarbon tail of a surfactant allows micellization to occur at a lower concentration due

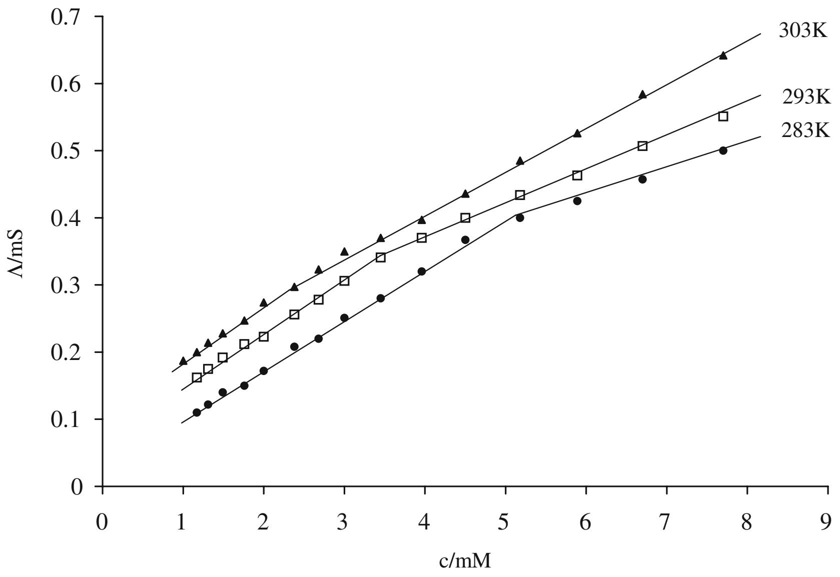

Fig. 2 Conductance, Λ, of AOT (Tetramenhylammonium salt) in aqueous solution as a function of the surfactant concentration at 283, 293, and 303 K

Table 1 Surface properties of AOT surfactants having different counterions (I^c) at various temperatures (T/K): cmc, maximum surface excess concentration, minimum areas per molecule at the surface

I^c	T/ K	cmc^a /(mol dm^{-3}×10^3)	Γ_{max}/mol cm^{-2}×10^8	A_{min}/ nm^2×10^2
Na^{+b}	283	3.55 (3.53)	1.42	1.17
	288	3.16 (3.20)	1.45	1.14
	293	2.88 (2.77)	1.49	1.11
	298	2.63 (2.40)	1.57	1.06
	303	2.24 (2.20)	1.76	0.94
	308	2.37 (2.26)	1.70	0.98
	313	2.80 (2.69)	1.71	0.97
NH_4^{+b}	283	3.87 (3.85)	1.56	1.06
	288	3.31 (3.20)	1.58	1.05
	293	3.09 (3.12)	1.45	1.14
	298	2.70 (2.65)	1.55	1.07
	303	2.59 (2.52)	1.80	0.92
	308	2.65 (2.60)	1.72	0.96
	313	2.82 (2.75)	1.76	0.94
$(CH_3)_4N^+$	283	4.76 (4.61)	1.68	0.99
	288	3.82 (4.10)	1.65	1.01
	293	3.24 (3.40)	1.53	1.08
	298	2.90 (2.90)	1.60	1.04
	303	2.05 (2.35)	1.80	0.92
	308	2.10 (2.20)	1.72	0.96
	313	2.26 (2.31)	1.67	0.99
$(C_2H_5)_4N^+$	283	1.88 (2.10)	1.44	1.15
	288	1.78 (2.00)	1.33	1.25
	293	2.95 (1.85)	1.46	1.14
	298	2.45 (2.50)	1.43	1.16
	303	2.31 (2.43)	1.76	0.94
	308	2.37 (2.50)	1.31	1.27
	313	2.56 (2.63)	1.41	1.12
$(C_3H_7)_4N^+$	283	1.18 (1.34)	1.67	0.99
	288	1.05 (1.20)	1.71	0.97
	293	0.93 (0.98)	1.85	0.89
	298	0.97 (0.95)	1.71	0.97
	303	0.92 (0.85)	1.77	0.94
	308	0.87 (0.90)	1.69	0.98
	313	0.74 (0.80)	1.93	0.86
$(C_4H_9)_4N^+$	283	1.04 (1.11)	1.32	1.26
	288	0.87 (0.91)	1.40	1.18
	293	0.80 (0.83)	1.42	1.17
	298	0.77 (0.80)	1.63	1.02
	303	0.75 (0.78)	1.82	0.91

[a] The values in the parenthesis represent cmc determined by conductivity method

[b] Values are taken from [25]

to increased hydrophobicity of the hydrocarbon tail [23]. But, the increased ionic size from $N^+(CH_3)_4$ to $N^+(C_4H_9)_4$ enhances the micellization tendency and eventually reduces the cmc. Here, the hydrocarbon exterior of the tetraalkyl ions undergoes hydrophobic interactions with the exposed hydrocarbon of the micelle surface and overcome steric hindrance. However, such a phenomenon is little or absent in the set of counterions viz., $N^+(CH_3)_4$, NH_4^+ and Na^+. In the absence of any appreciable hydrophobic interaction, NH_4^+ and Na^+ ions interact with the micellar head groups more strongly than $N^+(CH_3)_4$ ions due to their smaller sizes (hydration number 4.6 and 6.5, respectively [25]). Eventually, they lead to form micelle more readily via efficient charge screening than that of $N^+(CH_3)_4$ ions, and the systems yield low cmc values. But, in case of other tetraalkylammonium ions, as the bulkiness of the ion increases due to the presence of large alkyl groups, the hydrophobicity plays an important role causing increasingly micellization to occur at lower concentrations as has already been mentioned.

Figure 3 shows that the cmc of the surfactants follows a characteristic temperature dependency and passes through a minimum at the temperature range 298–308 K. With increasing temperature, the dehydration of $N^+(CH_3)_4$ ion perhaps becomes most pronounced among all the counterions and results in the highest slope in Fig. 3 at temperature <298 K. The variation of cmc with temperature shows good agreement with the empirical equation given by La Mesa [26]:

$$(\mathrm{cmc}-\mathrm{cmc}^*)/\mathrm{cmc}^* = |(T-T^*)/T^*|^{\gamma'} \tag{1}$$

Where cmc^* is the minimum value of cmc and T^* the temperature at the minimum with $\gamma' = 1.74 \pm 0.03$. It should be mentioned that the exponent γ' has no obvious physical meaning, but both cmc^* and the related temperature, in case of a particular surfactant, are the measure of the hydrophobic–hydrophilic balance of micelle. The position of the minimum has thermodynamic significance also. The minimum in cmc represents minimum in free energy of micellization.

Thermodynamic parameters

The temperature dependency of AOT micelles having different counterions also enables to determine the corresponding thermodynamic parameters of micellization. According to mass action or phase separation model [27, 28, 36], the standard free energy of micelle formation per mole of monomer of nonionic surfactants is expressed by well-known equation:

$$\Delta G_m^0 = \mathrm{RT\ In}\ X_{\mathrm{cmc}} \tag{2}$$

Where X_{cmc} is the value of cmc expressed in mole fraction. But, in case of ionic surfactant, the situation is somewhat different due to the counterion dissociation, and ΔG_m^0 should not be equivalent to that of the nonionic surfactant.

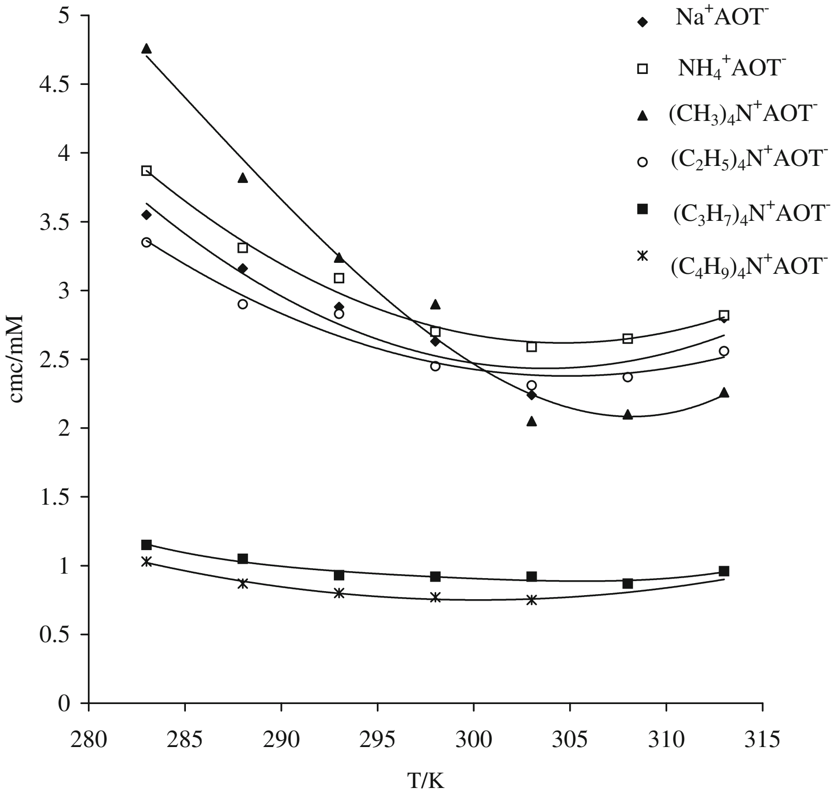

Fig. 3 Variation of cmc with temperature (K) of AOT having different counter cation

According to the theoretical mass action model, the micellization equilibrium for ionic surfactant can be expressed as:

$$xS^- + x\beta M^+ \rightleftharpoons (SM_\beta)_x^{-x(1-\beta)} \tag{3}$$

Where $(SM_\beta)_x$ is the micelle composed of x surfactant monomers and $x\beta$ counterions bearing S^- and M^+ as the monomer and counterion of the surfactant forming micelles. The value of β may correspond the fraction of bound counterion in the micelle. But, for nonionic surfactants, monomers and micelles are obviously uncharged, M^+ does not enter to the equation, and the model approaches to a limiting case having β=0. However, applying the mass action law to the monomer-micelle equilibrium for the ionic surfactant and taking into account the charges of counterion along with the other parameters, the Standard Gibbs free energy, ΔG_m^0 can be expressed as [29, 36]:

$$\Delta G_m^0 = (2 - \alpha)\mathrm{RT}\ \mathrm{In}\ X_{\mathrm{cmc}} \tag{4}$$

for an ionic uni-univalent surfactant. Here, X_{cmc} is the cmc expressed in mole fraction scale and $\alpha = 1 - \beta = \mathrm{p/n}$, is the ionization degree or counterionic ionization constant of the micelle, where p and n are the effective charge and the aggregation number of the micelle, respectively. The value of α can be determined from the ratio of the slope of the two linear fragments of conductivity–concentration plot above and below cmc [11, 30]. The values of ΔG_m^0 determined for each surfactant–counterion pair at different temperatures eventually give the standard enthalpy (ΔH_m^0) and entropy (ΔS_m^0) of micellization from the simple thermodynamic relations:

$$\Delta H_m^0 = -(2 - \alpha)\mathrm{RT}^2(\partial \mathrm{In}\ X_{\mathrm{cmc}}/\partial \mathrm{T})_{\mathrm{p}} \tag{5}$$

The Eq. 5 is obtained from the well-known Gibbs–Helmholtz relation and Eq. 4 assumes that α does not vary much with temperature**.** However, α is not strictly temperature independent and the more appropriate form of Eq. 5 should be

$$\begin{aligned} -\Delta H_m^0/\mathrm{T}^2 = {} & (2 - \alpha)\mathrm{R}(\partial \mathrm{In}\ X_{\mathrm{cmc}}/\partial \mathrm{T})_{\mathrm{p}} \\ & + \mathrm{R}\ \mathrm{In}\ X_{\mathrm{cmc}}(\partial(2 - \alpha)/\partial \mathrm{T}) \end{aligned} \tag{6}$$

Because the variation of α with temperature is not well defined and is devoid of any general trend, the quantity ∂(2–α)/∂T is difficult to find out experimentally [44]. Therefore, at least to gain qualitative information regarding the thermodynamics, Eq. 5 has been applied at the appropriate α.

$$\Delta S_m^0 = \left(\Delta H_m^0 - \Delta G_m^0\right)/\mathrm{T} \tag{7}$$

The ln X_{cmc} vs T plot is not linear. To evaluate ΔH_m^0, following polynomial form of variation of ln X_{cmc} with temperature has been considered.

$$\mathrm{In}\ X_{\mathrm{cmc}} = \mathrm{a} + \mathrm{bT} + \mathrm{cT}^2 \tag{8}$$

Where a, b, c are respective polynomial constants. Thus,

$$(\partial \text{In}\, X_{\text{cmc}}/\partial \text{T}) = \text{b} + 2\text{cT} \quad (9)$$

The polynomial constants b and c were evaluated from the fitting of experimental data. For all AOT surfactants with different counterions, the calculated thermodynamic parameters of micellization are listed in Table 2. Spontaneity of the micellization process is well explained from the large negative values of ΔG_m^0. Micelles containing the same amphiphile but different counterions show different values of thermodynamic parameters because of the counterions, which could be bound to a different extent and with different energy. Micellization in aqueous medium usually leads to a positive entropy change, which is mainly due to the melting of the "flickering cluster" that arises out of the hydrophobic effect of amphiphilic part of the surfactant molecules [24]. During formation of a micelle, the endothermic melting of the ordered polar solvent molecules around the nonpolar tail of AOT is greater than the subsequent exothermic association of the molecules. The resulting disordered state is actually reflected the positive entropy change. The variation of the standard thermodynamic parameters with different counterions at a certain temperature can also be explained by the size and the hydration of the counterion as has been already discussed. Like cmc, the ΔG_m^0 and ΔH_m^0 also show temperature

Table 2 Thermodynamic parameters of micellization for AOT surfactants with different counterions (I^c) at various temperatures: Standard Gibb's free energy, Enthalpy, and Entropy

I^{c}	T/C	$-\Delta G_m^0/(\text{kJ mol}^{-1})$	$-\Delta H_m^0/(\text{kJ mol}^{-1})$	$\Delta S_m^0/(\text{J K}^{-1}\text{ mol}^{-1})$
$\text{Na}^{+\text{b}}$	283	44.4	23.5	73.8
	288	37.2	25.3	41.3
	293	37.0	25.4	39.7
	298	32.1	22.1	33.3
	303	33.5	23.1	34.1
	308	33.6	23.8	32.0
	313	34.2	24.3	34.4
$\text{NH}_4^{+\text{b}}$	283	35.0	16.5	61.3
	288	33.0	15.6	56.9
	293	32.0	14.3	50.2
	298	32.5	15.9	56.6
	303	30.9	15.8	52.0
	308	34.1	16.0	50.0
	313	33.2	16.3	53.5
$(\text{CH}_3)_4\text{N}^+$	283	33.0	29.1	13.7
	288	34.2	30.0	14.6
	293	31.7	27.9	13.3
	298	30.8	27.2	12.1
	303	33.0	28.6	14.5
	308	32.3	28.5	12.2
	313	33.1	29.0	12.8
$(\text{C}_2\text{H}_5)_4\text{N}^+$	283	35.0	12.2	80.6
	288	33.0	11.7	74.0
	293	32.0	12.2	67.6
	298	32.5	12.3	67.8
	303	30.9	11.9	62.7
	308	34.1	13.3	67.5
	313	35.2	13.7	67.7
$(\text{C}_3\text{H}_7)_4\text{N}^+$	283	36.4	8.5	98.7
	288	34.7	8.1	92.3
	293	35.8	8.5	93.3
	298	36.6	8.8	93.1
	303	36.6	8.9	91.2
	308	35.4	8.7	86.5
	313	36.8	8.8	90.6
$(\text{C}_4\text{H}_9)_4\text{N}^+$	283	36.6	14.4	78.4
	288	37.6	14.9	78.8
	293	38.2	15.3	78.2
	298	34.4	15.2	64.4
	303	37.7	15.5	73.3

[b] Values are taken from [25]

dependency, and the profile passes through minima when these parameters are plotted against temperature for all the surfactant–counterion systems.

A close look on the thermodynamic parameters (Table 2) support the view that in order to form micelle, the gain in entropy is the major factor leading to negative change in Gibbs free energy [32–34] if the temperature is not very high. But the fact that though the free energy changes are not very different, the enthalpy change is significantly higher and the entropy changes are much lower for $N^+(CH_3)_4$ counterion containing AOT compared to all other systems. This leads one to interpret that the enthalpy contributes major driving force in micellization. Loosely bound water dipole with the $N^+(CH_3)_4$ ion may cause lower contribution of ΔS_m^0 in aggregation process. However, like a variety of processes such as oxidation–reduction, hydrolysis, protein unfolding, etc., micellization process also exhibit a linear relationship between the enthalpy and entropy change, which is known as enthalpy–entropy compensation [35–37]. This is important in connection with the hydrophobicity of surfactant which leads to stable micelle formation. In general, the compensation phenomenon between the enthalpy change ΔH_m^0 and the entropy change ΔS_m^0 in various processes can be described in the form of [36, 42]

$$\Delta H_m^0 = \Delta H_m^* + T_c \Delta S_m^0 \qquad (10)$$

In a plot of ΔH_m^0 vs ΔS_m^0, the slope T_c has a dimension of temperature and is known as compensation temperature. This can be interpreted as a measure of desolvation part of micellization, that means a characteristic of solute–solute and solute–solvent interaction, and the intercept characterizes the solute–solute interaction. Our experimental results also show a good agreement with the enthalpy–entropy compensation linearity for all AOT surfactants having different counterions. Figure 4 represents enthalpy–entropy compensation plot at 298 K. The calculated compensation temperature value of 295.6 K satisfactorily follows the characteristic range of other ionic surfactants [36–38]. The intercept, ΔH_m^*, has been calculated as −32.8 k Jmol^{-1}, which corresponds the driving force of micellization where the entropy does not contribute the process at a particular temperature (298 K).

It is well known that the air–solution interface of a surfactant solution is well populated by the adsorbed molecules. The Γ_{max} and A_{min} in the aqueous–air interface are calculated by using the following relations [39–41].

$$\Gamma \max = (1/2.303 n' RT)(-\partial\gamma/\partial \log C) \qquad (11)$$

$$A_{min} = 1/(N\Gamma) \qquad (12)$$

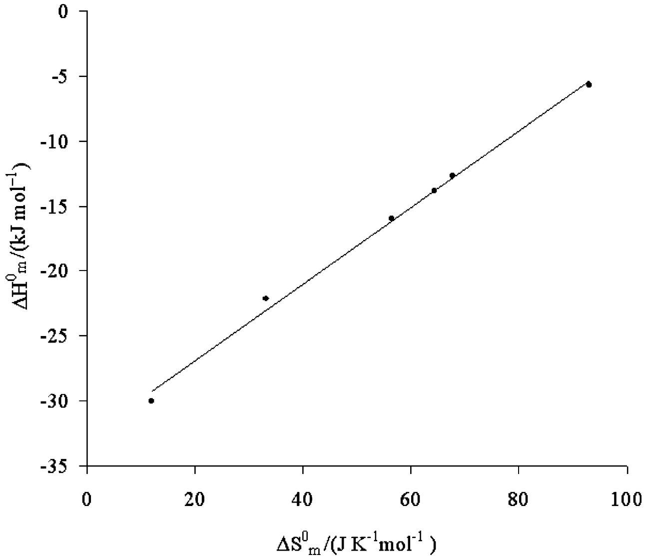

Fig. 4 Enthalpy–entropy compensation plots for AOT surfactants having different counterions at 298 K

Where γ expresses the surface tension, N is the Avogadro number, C and n' are the concentration and number particles per molecule of the surfactant, respectively. Because in aqueous solution at concentrations less than cmc, the AOT behaves like a uni-univalent electrolyte, the thermodynamic treatment requires $n'=2$, states an equimolar ratio of surfactant anion and counterion in the interface. Similar to analysis of ln X_{cmc} vs T plot, γ vs ln C plot was also fitted to a second order polynomial to measure Γ_{max}. It is well known that for both nonionic [40] and anionic [41] surfactants, Γ_{max} values slightly decreases with temperature while in some other cases, an increase of the surface excess quantity has been reported [43] in presence of additives. In the case of present AOT surfactant with six different counterions, the change of Γ_{max} does not follow the regular trend. A critical examination of Table 2 shows a slight increment in Γ_{max} with temperature for all the counterions, which may be due to the effect of lower hydration of the sulfosuccinate of AOT at higher temperature and, hence, an increasing tendency to move to the air–liquid interface. It is quite obvious that the standard state for the adsorbed surfactant is a hypothetical monolayer at its minimum surface area per molecule but at zero surface pressure. The typical double chain of the amphiphile may also partially be responsible for this result causing "steric inhibition" during adsorption. The moderate increase in the effectiveness of adsorption at the air–water interface with temperature is due to increased thermal motion, and therefore, A_{min} displays an inverse trend with temperature, as expected. With increasing bulkiness of the counterions of the amphiphiles, the increase of Γ_{max} are quite noticeable. At a particular temperature, Γ_{max} shows anomalous behavior as the counterion of the surfactant changes. It may be attributed to the enhanced hydrophobicity of the anionic part of the surfactant molecules depending upon accessibility of their corresponding counterions. A study of the behavior of tetramethylammoniumdodecyl sulfate at the air–solution interface indicated to a penetration of a part of the $N^+(CH_3)_4$ ions in the dodecyl sulfate layer [31]. A similar phenomenon may also partially be responsible for the observed surface behavior in the present system.

Conclusion

The sizes of tetraalkylammonium counterions influence cmc of AOT surfactant in aqueous solution significantly. As the size of counterion increases from $N^+(C_2H_5)_4$ to $N^+(C_4H_9)_4$, the cmc value decreases due to increase in the hydrophobic interaction of counterions with the exterior of the micelle. The set of counterions viz., NH_4^+, Na^+, and $N^+(CH_3)_4$ yield higher cmc value due to little or no hydrophobic interaction with the micelle. The NH_4^+ and Na^+ ions, on the other hand, interact with micellar head group more strongly than $N^+(CH_3)_4$ ion for their small sizes, and consequently, the cmc values of NH_4-AOT and Na-AOT are low compared to $N(CH_3)_4$-AOT due to efficient charge screening of the head group. The values of standard thermodynamic parameters indicate spontaneity of micelle formation, and their order could be well explained in terms of bulkiness and nature of hydration of the counterion together with hydrophobic and electrostatic interactions. Characteristic temperature dependency of cmc is observed in almost all the systems with the appearance of a shallow minimum in each case. The striking steep fall of cmc's of $N(CH_3)_4$-AOT with temperature manifests in the large ΔH_m^0 values, which leads to low entropy changes. Loosely bound water dipoles with the $N^+(CH_3)_4$ counterions may cause lower contribution of ΔS_m^0 to the aggregation process.

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