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ORIGINAL CONTRIBUTION

Mandeep Singh Bakshi
Navjot Kaur
Rakesh Kumar Mahajan
Jasmeet Singh
Narpinder Singh

Estimation of degree of counterion binding and related parameters of monomeric and dimeric cationic surfactants from cloud point measurements by using triblock polymer as probe

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M. S. Bakshi (✉) · N. Kaur ·
R. K. Mahajan · J. Singh
Department of Chemistry,
Guru Nanak Dev University,
Amritsar 143005, Punjab, India
e-mail: ms_bakshi@yahoo.com

N. Singh
Department of Food and Technology,
Guru Nanak Dev University,
Amritsar 143005, Punjab, India

Abstract The cloud point (C_P) measurements of aqueous solutions of a triblock polymer (TBP) [$(PEO)_{2.5}(PPO)_{31}(PEO)_{2.5}$], in the presence of varying amounts of cationic surfactants (monomeric and dimeric alkylammoniumbromides) covering premicellar to postmicellar regions, have been carried out. A plot of C_P vs surfactant concentration allowed us to evaluate apparent critical micelle concentration (cmc*), which has been found to decrease with an increase in the amount of salt. The cmc* values thus obtained in the absence and presence of salt allowed us to evaluate counterion binding (β) by using the Corrin–Harkins method. β values have been further used to evaluate the thermodynamic parameters of these ionic surfactants. The results suggest that the β values evaluated using this method, especially at low [TBP], are in good agreement with those already reported in the literature.

Keywords Cloud point measurements · Counterion binding · Triblock polymers · Ionic surfactants · Thermodynamic parameters

Introduction

Micelle formation process, in the case of ionic surfactants, takes place in a delicate balance between hydrophobic and hydrophilic forces. The free energy of micelle formation is a favorable contribution of hydrophobic interactions and is an unfavorable contribution of electrostatic interactions operating at the micelle–solution interface. Head group repulsions existing in the Stern layer of micelles are the main micelle-destabilizing factors and contribute to positive free energy. The adsorption of oppositely charged counterions at the micelle–solution interface reduces this repulsion and allows the predominance of hydrophobic interactions in order to achieve micelle formation. Thus, the degree of counterion binding (β) is an important parameter that governs the stability of micelles. Several methods exist to evaluate β; the present method is based upon cloud point (C_P) measurements and it works very nicely [1] when a small amount of triblock polymer (TBP) is used as a probe.

In the case of the present method, the C_P of TBP at its fixed concentration varies nonlinearly with respect to an increase in ionic surfactant concentration from the premicellar to the postmicellar range in aqueous solutions. C_P data can very well fit into two linear equations corresponding to premicellar and postmicellar regions, and intersect at a certain point that has been found to be quite close to the critical micelle concentration of that surfactant. This apparent critical micelle concentration (cmc*) thus obtained can be used to evaluate β values from well-known Corrin–Harkins plots.

Experimental

Materials

The TBP [$(PEO)_{2.5}(PPO)_{31}(PEO)_{2.5}$] was obtained from Aldrich and was used without further purification. Dodecyltrimethylammonium bromide (DTAB), tetradecyltrimethylammonium bromide (TTAB), and hexadecyltrimethylammonium bromide (HTAB) (all obtained from Lancaster Synthesis, UK) were used as received. The dimeric cationic surfactants dimethylene bis(dodecyldi-

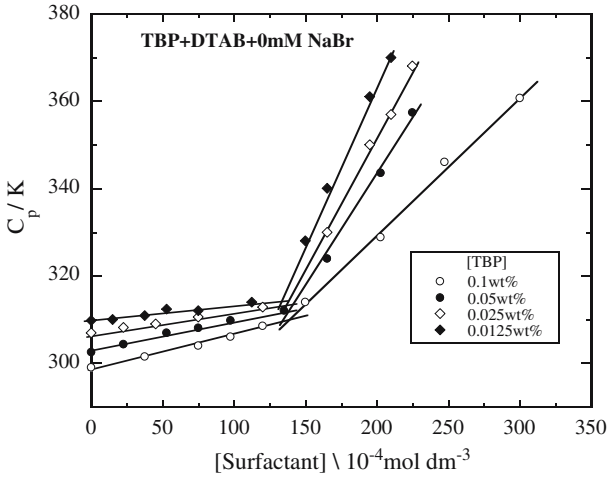

Fig. 1 Plot of C_P vs [surfactant] for TBP + DTAB, in the absence of NaBr at different fixed [TBP]

methylammonium bromide) (12-2-12) and dimethylene bis (tetradecyldimethylammonium bromide) (14-2-14) were synthesized as reported in the literature [2] and were fully characterized and purified before use.

C_P measurements

The C_P (essentially below 100°C) values of TBP + ionic surfactant + water ternary mixtures in the presence as well as in the absence of NaBr were measured by suspending glass tubes in an oil bath, whose temperature was increased gradually with constant stirring. The C_P was determined by visual observations of an abrupt change in the appearance of surfactant solution from clear to the first appearance of turbidity. The samples were heated at a rate of about 0.1°C min^{-1} after the temperature had reached a few degrees below the pre-estimated C_P temperature. After the temperature had exceeded the C_P, the sample was cooled below the C_P temperature and then was heated again to check the reproducibility of measurements. The maximum uncertainty in the C_P measurements was within ±0.2°C. In all ternary mixtures, the concentration of TBP was kept constant, and four levels of concentrations (i.e., 0.1, 0.5, 0.025, and 0.0125 wt%) were maintained. At each level, a series of solutions was prepared by increasing the concentration of ionic surfactants in such a way that both premicellar and postmicellar regions could be covered. Then, a constant amount (i.e., 2 ml) of each sample was taken in a number of stoppered glass tubes to determine the C_P. Similar experiments were carried out in aqueous salt

Table 1 Values of cmc* (10^{-4} mol dm^{-3}) and C_P (K) of various surfactants in aqueous TBP solutions in the absence as well as in the presence of NaBr from C_P measurements

[TBP] (wt%)	DTAB		TTAB		HTAB	
	cmc*	C_P	cmc*	C_P	cmc*	C_P
0.00[a]	145 [14] 152 [15] 160 [4]		38.3 [15]		10.0 [15] 9.2 [16]	
0.0125	136±6.8	314.0	34.0±1.7	319.2	6.2±0.31	320.2
0.025	138±6.9	312.4	35.0±1.7	315.0	7.5±0.37	317.9
0.05	139±6.9	311.2	36.0±1.8	309.6	10.5±0.52	314.2
0.1	140±7.0	310.0	36.6±1.8	306.5	14.5±0.72	311.0
10 mM NaBr						
0.0125	58.0±2.9	321.0	13.3±0.66	327.0	3.6±0.18	326.0
0.025	68.2±3.4	318.2	17.2±0.86	319.8	4.8±0.24	323.8
0.05	72.2±3.6	316.6	19.0±0.95	312.0	10.0±0.50	315.2
0.1	87.3±4.3	313.0	20.0±1.0	308.0	15.0±0.75	311.4
20 mM NaBr						
0.0125	52.4±2.6	322.6	9.0±0.45	329.0	2.2±0.11	327.0
0.025	62.0±3.1	319.6	11.3±0.56	323.0	3.0±0.15	324.0
0.05	65.3±3.2	318.0	13.0±0.65	314.0	6.8±0.34	316.0
0.1	79.0±3.9	314.0	13.9±0.69	309.0	10.0±0.50	313.0
30 mM NaBr						
0.0125	47.5±2.3	324.8	6.0±0.30	329.0	1.5±0.07	328.0
0.025	56.6±2.8	322.0	8.0±0.40	323.0	2.0±0.10	325.4
0.05	60.0±3.0	320.4	9.0±0.45	316.8	5.0±0.25	318.0
0.1	71.5±3.5	316.61	0.0±0.50	308.0	7.8±0.39	314.0

[a]Values in pure water

Table 2 Values of cmc* (10^{-4} mol dm^{-3}) and C_P (K) of various surfactants in aqueous TBP solutions in the absence as well as in the presence of NaBr from C_P measurements

[TBP] (wt%)	12-2-12		14-2-14	
	cmc*	C_P	cmc*	C_P
0.00[a]	8.4 [17]		2.0	
	8.6 [18]			
0.0125	8.0±0.40	323.0	2.0±0.10	334.0
0.025	8.5±0.42	317.6	3.2±0.16	320.0
0.05	9.0±0.45	314.2	5.4±0.27	311.0
0.1	12.0±0.60	309.0	6.0±0.30	308.0
10 mM NaBr				
0.0125	3.6±0.18	324.0	1.25±0.06	335.0
0.025	6.0±0.30	319.0	1.80±0.09	326.8
0.05	8.2±0.41	315.0	4.90±0.24	314.2
0.1	8.9±0.44	311.2	5.80±0.29	310.0
20 mM NaBr				
0.0125	3.0±0.15	327.0	1.1±0.55	336.0
0.025	5.4±0.27	323.0	1.5±0.07	330.0
0.05	7.2±0.36	319.0	3.9±0.19	316.0
0.1	8.4±0.42	312.0	4.6±0.23	313.3
30 mM NaBr				
0.0125	2.8±0.14	329.0	1.0±0.05	338.0
0.025	5.0±0.25	324.0	1.4±0.07	331.8
0.05	6.6±0.33	321.0	3.5±0.17	317.0
0.1	8.0±0.40	313.2	4.0±0.20	315.0

[a]Values in pure water

(NaBr) solutions, instead of pure water, by again keeping the concentrations of both TBP and NaBr constant. Such solutions now consist of four components (i.e., TBP + ionic surfactant + water + NaBr) and, again, four levels of constant [NaBr] (i.e., 0, 10, 20, and 30×10^{-3} mol dm^{-3}) were maintained at each constant level of TBP. The clouding temperature of each sample, both in the absence as well as in the presence of NaBr for a series of surfactant solutions, was noted down.

Results and discussion

Critical micelle concentration and counterion binding

Figure 1 shows the C_P data with respect to surfactant concentration in a salt-free system for DTAB + TBP, while similar plots were observed for all other mixtures, at four different fixed TBP concentrations. Each C_P curve shows that, initially, there is a slight increase in C_P with an increase in the amount of each surfactant, which, thereafter at a certain surfactant concentration, increases instantaneously. The initial slight increase in the C_P value can be related to the induction of surfactant monomers in TBP micelles, which makes TBP micelles more hydrated due to the presence of water molecules in the hydration spheres of

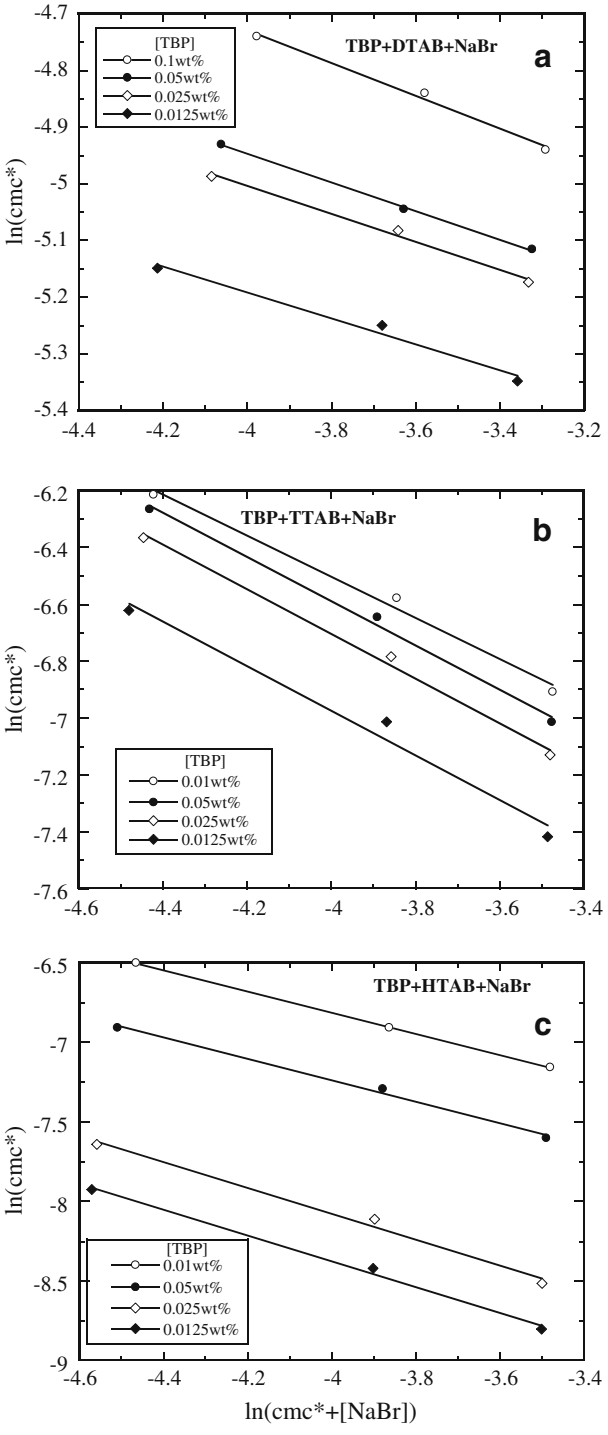

Fig. 2 Corrin–Harkins plots for **a** TBP + DTAB, **b** TBP + TTAB, and **c** TBP + HTAB at various fixed [TBP]

both ionic head groups of cationic surfactants as well as their counterions. However, a further increase in surfactant concentration leads to the micellization of ionic surfactants. This, in return, facilitates the solubilization of TBP in ionic micelles and, hence, is responsible for an instant increase in

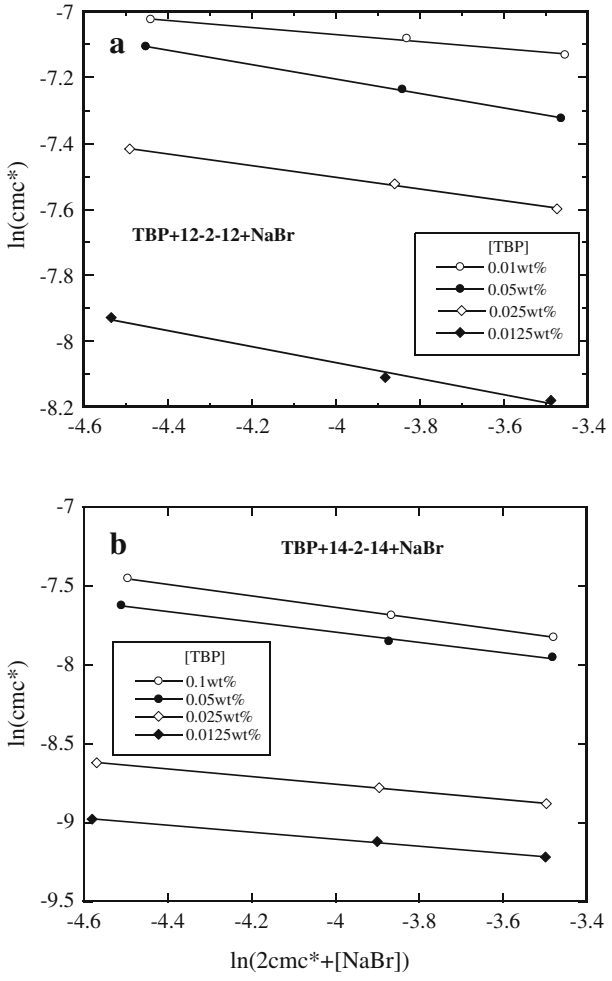

Fig. 3 Corrin–Harkins plots for **a** TBP + 12-2-12 and **b** TBP + 14-2-14 at various fixed [TBP]

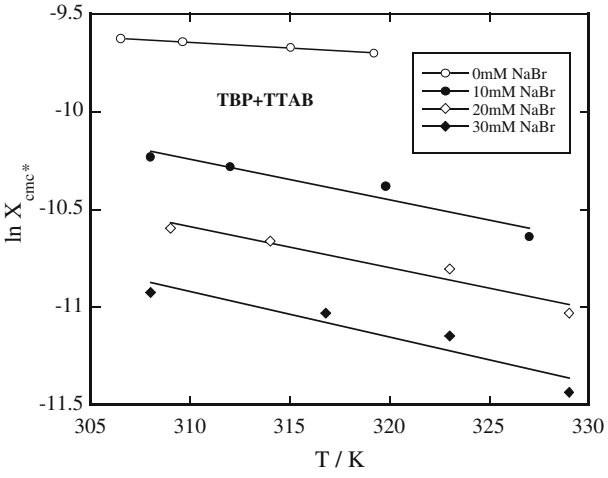

Fig. 4 Plot of ln X_{cmc*} vs T (essentially the C_P) for TBP + TTAB + NaBr at different fixed [NaBr]. The *points* at each line represent the data at four different TBP concentrations

C_P [3]. The break in C_P curve, therefore, represents the cmc* value of each surfactant in the almost TBP-free aqueous phase, since most of the TBP is expected to be precipitated. Tables 1 and 2 list the cmc* values thus obtained at the respective C_P temperatures. These values at low [TBP] are quite close to the one in pure water taken from the literature. However, a further increase in [TBP] results in an increase in cmc* in almost all cases. This can be attributed to the presence of some amount of TBP left in the aqueous micellar solution even after its precipitation and may reduce the overall dielectric constant of the aqueous phase. Hence, TBP can be used as a probe for the determination of cmc* via C_P measurements when used in the minimum possible amount.

Similarly, the cmc* values for each monomeric and dimeric surfactant have also been obtained from C_P data at different fixed levels of NaBr concentrations and are listed in Tables 1 and 2. One can see that cmc* decreases with an increase in [NaBr] at a particular fixed [TBP]. Reduction in cmc* with an increase in constant [NaBr] is due to the salting-out effect of NaBr because of the adsorption [4] of excess counterions at the charged micelle–solution interface, thus reducing polar head group repulsions. Therefore, the variation in C_P can be related to the total counterion

Table 3 Values of β for DTAB, TTAB, HTAB, 12-2-12, and 14-2-14 at different [TBP]

[TBP] (wt%)	β				
	DTAB	TTAB	HTAB	12-2-12	14-2-14
0.00[a]	0.20 [17]	0.80 [19]	0.83 [19, 20]	0.16 [17] 0.18 [22]	0.16 [21]
0.0125	0.22±0.01	0.78±0.04	0.81±0.04	0.24±0.02	0.22±0.01
0.025	0.24±0.02	0.78±0.04	0.81±0.04	0.17±0.01	0.24±0.01
0.05	0.25±0.01	0.77±0.04	0.67±0.03	0.21±0.01	0.32±0.02
0.1	0.28±0.02	0.72±0.03	0.66±0.03	0.11±0.01	0.36±0.02

[a]Values in pure water

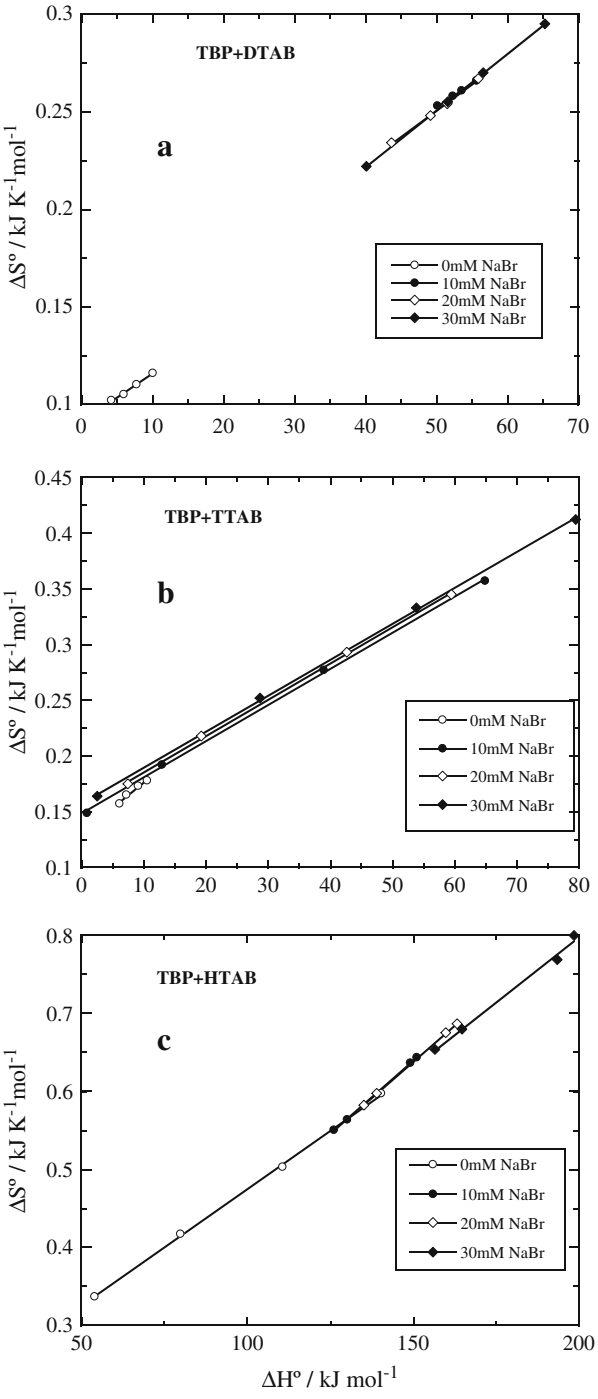

Fig. 5 Plots of $\Delta S°$ vs $\Delta H°$ for **a** TBP + DTAB, **b** TBP + TTAB, and **c** TBP + HTAB at different fixed [NaBr]

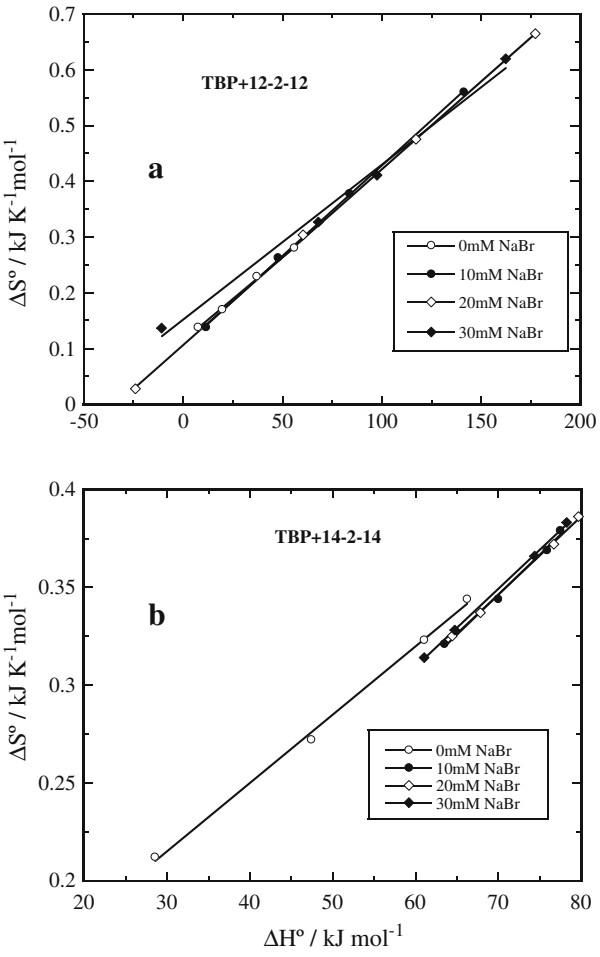

Fig. 6 Plots of $\Delta S°$ vs $\Delta H°$ for **a** TBP + 12-2-12 and **b** TBP + 14-2-14 at different fixed [NaBr]

concentration from which one can evaluate β by using the mass action model [5, 6]. It is given by the following equilibria between the surfactant monomers, counterions, and micelles for monomeric and dimeric cationic surfactants, respectively:

$$nS^{+} + mG^{-} \leftrightarrow M^{+(n-m)} \qquad (for\ monomeric) \tag{1}$$

$$nS^{2+} + mG \leftrightarrow M^{+(2n-m)} \qquad (for\ dimeric) \tag{2}$$

where S^{+}, G^{-}, and M^{+} indicate the monomeric surfactant, counterion, and micelle species, respectively. From these equilibria equations, the dependence of cmc* on the counterion concentration (i.e., Br^{-}) can be given by the following relation:

$$ln(cmc^{*}) = -(m/n)lnC_{Br-} + constant \tag{3}$$

The logarithm of cmc* to the logarithm of free counterion concentration is known as the Corrin–Harkins plot [7–9]. It is to be mentioned here that these equilibria in the case of present surfactants have been considered in aqueous TBP solutions, since the concentration of TBP at the

C_P left in the aqueous phase is assumed to be negligible. Apart from this, the temperature and [TBP] dependence of the cmc* values evaluated from the C_P data for a particular surfactant have been neglected, since they vary within a very narrow temperature range.

Figures 2 and 3 show the Corrin–Harkins plots of present monomeric and dimeric surfactants at fixed TBP concentrations. A good linear variation can be observed in all cases, and the slope of each line gives the value of counterion binding (β=m/n). β values thus computed for each surfactant at different TBP concentrations are listed in Table 3. Table 3 also lists the β value in pure water (i.e., [TBP]=0 mol dm^{-3}) for all surfactants in the first row of data. This is to compare these values evaluated from other studies with the present ones. A close inspection of various columns of Table 3 demonstrates that the β value of each surfactant in pure water is mostly close to the values determined using the present method. Table 3 also indicates that there is little variation in the β value for each surfactant, especially at low [TBP]. Thus, on the whole, it can be said that this method works well to determine the β value for ionic surfactants using TBP as a probe, and more authentic values can be obtained at lower TBP concentrations.

Thermodynamic parameters

Parameters of micellization of the present surfactants, such as standard Gibbs free energy ($\Delta G°$), standard enthalpy ($\Delta H°$), and standard entropy change ($\Delta S°$), have been calculated in aqueous TBP solution in the absence as well as in the presence of NaBr. There are several approaches [10–12] to the problem of transforming cmc values into standard free energies. For ionic systems, free energy includes a contribution of the involvement of the counterion with the micelle. This contribution can be taken into account either by a chemical approach, based on the binding of some counterions to the micelles, or by a physical approach, using an electrostatic calculation based on a fully ionized model. Application of the chemical approach is based on phase separation models or mass action models. The former is based on an assumption that a separate phase appears at cmc, while the latter demonstrates an association–dissociation equilibrium among micelles and unassociated monomers. In both cases, the $\Delta G°$ change involved the transfer of 1 mol of amphiphile from the solution to the micellar phase. In the present study, this change takes place in an aqueous TBP solution. In the case of ionic surfactants, $\Delta G°$ is given by the following relation:

$$\Delta G^\circ = (1+\beta) RT ln X_{cmc^*} \tag{4}$$

where R is the gas constant, T is the absolute temperature, X_{cmc*} is the cmc* in mole fraction units, and β is the counterion binding evaluated from the C_P measurements, as mentioned in the previous section. Here, we assume that the concentration of the monomeric surfactant, along with the micelles, remains constant and equal to the cmc in the case of the phase separation model. T is the clouding temperature (C_P) (Tables 1 and 2) at the cmc. By considering the mass action model, the $\Delta H°$ of each ionic surfactant in aqueous TBP solution in the absence as well as in the presence of NaBr can be evaluated by applying the Gibbs–Helmholtz equation in the following form:

$$\Delta H^\circ = -(1+\beta) RT^2 \left(\frac{\partial \ln X_{cmc^*}}{\partial T} \right)_P \tag{5}$$

Since $\Delta H°$ is not constant with respect to the temperature, it is thus obtained by using the following polynomial equation through Eq. 5:

$$ln\, X_{cmc^*} = a + bT + cT^2 \tag{6}$$

The plots of ln X_{cmc} vs T (here, T is also C_P) are shown in Fig. 4 for TTAB as representative example. By using $\Delta G°$ and $\Delta H°$, $\Delta S°$ can be evaluated from the following equation:

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T \tag{7}$$

A variation in $\Delta G°$ value (not shown) for all surfactants in the presence of constant amounts of TBP suggests that it becomes more negative with an increase in [NaBr] at a particular fixed [TBP]. This indicates the facilitation of the micellization of each surfactant in the presence of salt, which can obviously be understood on the basis of reduction in polar head group repulsions. On the other hand, $\Delta G°$ values become less negative with an increase in [TBP] at a constant level of NaBr concentration. It means that the increase in the amount of TBP practically delays the micelle formation of ionic surfactants in aqueous phase. This aspect has already been discussed with respect to an increase of cmc* of ionic surfactants with an increase in the amount of TBP concentration, which suggests that some TBP monomers get solubilized in ionic micelles. The latter

Table 4 Values of T_c (K) for DTAB, TTAB, HTAB, 12-2-12, and 14-2-14 at different [NaBr] in aqueous TBP

	T_c				
[NaBr] (10^{-3} mol dm^{-3})	DTAB	TTAB	HTAB	12-2-12	14-2-14
In water				305.7 [23] 321.5	
0.00	405.64	237.62	335.52	334.75	286.20
10.0	420.02	306.28	268.46	309.01	244.60
20.0	373.13	311.26	268.30	316.22	250.72
30.0	344.13	314.04	299.20	360.33	250.63

effect would lead to an increase in cmc* (Tables 1 and 2), since TBP is always less hydrophobic than ionic surfactants. Thus, the induction of TBP in ionic micelles would reduce the overall hydrophobicity, which is the driving force for micellization. Despite the dependence of cmc* on [TBP], this method to evaluate β from C_P measurements works well at low [TBP], where a good comparison can be seen with literature values (Table 3).

The variation of both $\Delta H°$ and $\Delta S°$ values follows the mutual relationship of enthalpy–entropy compensation phenomenon. When the enthalpy term contributes less to free energy, its counterpart, the entropy term, contributes more in order to lead free energy to become a large negative value, and vice versa. Figures 5 and 6 show such a relationship for the present ionic surfactants. All $\Delta H°$–$\Delta S°$ compensation phenomena demonstrate good linear behaviors. There are several reports for nonionic, anionic, and cationic surfactants in which a good linear relationship between $\Delta H°$ and $\Delta S°$ values has been observed with a slope of 1/307 (K^{-1}). The latter is known as compensation temperature (T_c), which has practically no significant meaning but is a geometrical mean of a range of temperatures for a particular system. Such a linearity between $\Delta H°$ and $\Delta S°$ can be expressed by the following empirical equation:

$$\Delta S^\circ = (1/T_c)\Delta H^\circ + \sigma \tag{8}$$

where $(1/T_c)$ is the slope and σ is the intercept of linear plots. The T_c values thus obtained for all present surfactants are listed in Table 4 at different [NaBr]. These values in pure water for the present surfactants have also been mentioned for the sake of comparison. It is to be noted that T_c ranges from 299 to 315 K, depending on the nature of species [13]. Table 4 demonstrates that the T_c values for the present surfactants show a regular increase with an increase in the amount of NaBr, except in case of DTAB. One can see that these values at NaBr=0 mol dm^{-3} are closer to the range specified for ionic surfactants.

Conclusions

The results of the present work justify the method of the determination of β values from C_P measurements of TBP for various ionic surfactants. It has been observed that this method works well to determine the β value at the lowest possible [TBP], where the TBP has a minimum interference in the micellization process of ionic surfactants. The β values thus obtained for various monomeric as well as dimeric surfactants are quite close to the values reported in the literature, thus demonstrating a good applicability of this method. Therefore, it can be said that the present method can give even better results by choosing an appropriate TBP whose minimum concentration would be required to determine the β value.

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