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Studies on aggregation and counterion binding nature of didodecyldimethylammonium bromide in presence of added salts

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The critical micelle concentration of double chained cationic surfactant didodecyldimethylammonium bromide (DDAB) are determined in the presence of added counterions, viz., bromide, chloride and, benzoate, using surface tension, conductance and fluorescence methods. The main highlight of the article is the existence of two break-points in the surface tension isotherms of DDAB, depending on the type and amount of added counterion. At some concentrations of added counterions, normal surface tension behavior is also observed with only one break-point in the surface tension isotherm. The variation in the cmc value of DDAB with counterion concentration is studied using well-known Corrin-Harkins and modified Corrin-Harkins equations. The information gathered about the aggregation behavior of DDAB in the presence of added counterions is expected to be useful in view of DDAB's wide utility in commercial, chemical and pharmaceutical field.

Keywords: Solution chemistry, Aggregation behavior, Critical micelle concentration, Surface tension, Corrin-Harkins equation, Counterion binding, Surfactants, Cationic surfactants, didodecyldimethylammonium bromide

Surfactants are amphiphillic molecules composed of polar hydrophilic and non-polar hydrophobic portions that self-assemble to form aggregates of different geometries in the chosen media above a certain concentration known as critical micelle concentration. Vesicle is one such aggregate geometry formed by some surfactants and is considered to be an important microstructure as it mimics the biological cell membrane and is also used as microreactors, drug carrier, etc. Didodecyldimethylammonium bromide (DDAB) is a double-chain cationic surfactant which organizes instantly into bilayers like vesicles and liposome.[1] DDAB has diverse phase behavior[2] and it tends to swell in water to form two L_α phases.[3] In dilute aqueous solutions of DDAB (less than 3 wt%), a biphasic solution consisting of swollen lamellar crystallites dispersed in a metastable sponge phase (L_3) is formed, which eventually becomes an isotropic micellar solution.[4,5] Changing the native counterion (bromide) to hydroxide (DDAOH) or acetate (DDAAc) renders higher aqueous solubility of these surfactants, forming clear solutions even up to 1 *M*. The nature of morphology of the aggregates is found to be mainly vesicles and micelles whereas the L_α phase is formed only at higher concentrations.[6-13] The effect of monovalent (Cl^-) and divalent (SO_4^{2-}) counterions on the solubility and swelling properties of DDA^+ in aqueous medium is almost similar to that of Br^-.[14,15] This study is consistent with the trend observed for a different cationic surfactant, namely, alkyltrimethylammonium systems.[11] Recently, a detailed study on extensive range of microstructures of DDA^+ surfactants with hydrolyzable counterions, viz., phosphate and oxalate and bicarbonate counterions, was reported.[16] Such variation in the phase behavior is explained in terms of counterion binding to DDA^+ headgroups. There are plenty of papers in the literature where all the studies reported on the behavior of DDA^+ surfactants was observed with respect to native counterions.

To the best of our knowledge, there has been no attempt to study the effect of added counterion concentrations on the aggregation and counterion binding behavior of DDAB. Therefore we have made an attempt to study the binding behavior of DDAB in the presence of added salt concentrations and calculated the related binding parameter. In addition, Corrin-Harkins (CH) equation[17] is a thermodynamically based method to calculate the counterion binding constant in presence of increasing salt concentrations by taking into account only the cmc values. Normally, the applicability of the CH relation has been found to be limited in the salt concentration range where salting-out effect is negligible, smaller than 0.1-0.2 *M* of added univalent salts.[17] In the CH relation the counterion is assumed to be common for both the surfactant and the added salt. We reported the limitation of the CH equation to determine the counterion binding constant (β) for ionic surfactants in presence of mixed added counterions from the salt different from that of surfactant's native counterion.[18-20] Now, herein we present a detailed study on the effect of three counterions, viz., bromide, chloride and benzoate on the aggregation behavior of DDAB in aqueous medium with respect to its cmc, counterion binding and hydrodynamic radius keeping in view the significance of such study due to DDA^+ based surfactant's wide applications in commercial, chemical and pharmaceutical field.[21-23] The present studies explore mainly the change in binding nature of DDAB initially with the addition of small amount of added salt which might leads to the change in morphological transition of DDAB aggregates.

Materials and Methods

DDAB (Fluka, ≥ 98%), NaBr (Merck, >99.5%), NaCl (Merck, > 99.5%), sodium benzoate (Fluka, > 99.5%), pyrene (Fluka) were used without purification. Milli-Q grade water was used for preparing solutions.

Surface tension measurements were made by the Wilhelmy plate method using a K11 Krüss tensiometer. Conductance measurements were made at 1 kHz using a B905 Wayne Kerr Automatic Precision bridge and a dip-type conductivity cell with platinized platinum electrodes. The cell constant was determined using standard KCl solution. The fluorescence emission spectra of pyrene excited at 335 nm were recorded on a Hitachi 4500 FL spectrophotometer. The temperature of the sample during conductance, surface tension and fluorescence measurements was maintained at 25 ºC by using a Haake DC 10 circulation bath. Dynamic light scattering (DLS) measurements were made at 25 °C using a Malvern Zetasizer Nano ZS instrument operating at 633 nm (4 mW He-Ne laser was 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) of aggregates in each sample.

Results and Discussion

Nature of surface tension isotherm

In Fig. 1 variation of surface tension (γ) of aqueous DDAB solution with DDAB concentration is shown. Two breaks can be seen in the surface tension profile, one at *ca.* 6.3×10^{-5} mol kg^{-1} and another 15.8×10^{-5} mol kg^{-1}, which are in good agreement with the previously reported data.[24-28] The first and second breaks in the surface tension isotherm of DDAB are attributed to the formation of DDAB micelles and vesicles, respectively.[27, 29] The existence of two breaks in the surface tension isotherm is also reported in several other mixed systems containing DDAB, for example, in the DDAB/DTAC/water[28,30-31] and DDAB/SDBS/water[32] systems, where DTAC and SDBS refer to dodecyltrimethylammonium chloride and sodium dodecylbenzenesulfonate, respectively. In order to examine the effect of added salt on the two breaks in the surface tension isotherm of aqueous DDAB solution, surface tension measurements of DDAB were made in aqueous NaBr, NaCl and NaBz solutions.

DDAB-NaBr

Representative plots of the variation of surface tension of DDAB solutions with increasing surfactant concentration in the presence of NaBr are shown in Fig. 2. DDAB shows normal surface tension curve with only one prominent break point at a low concentration of 0.35 mol kg^{-1} of added NaBr. But two transition points can be seen in the γ versus log [DDAB] curves in presence of NaBr similar to that in water (Fig. 1) at higher concentration of added NaBr. The γ values rapidly decreases up to the first transition/break point at 'a', then decrease gradually above it and becomes constant above second break point at 'b'. As mentioned above, in the case of

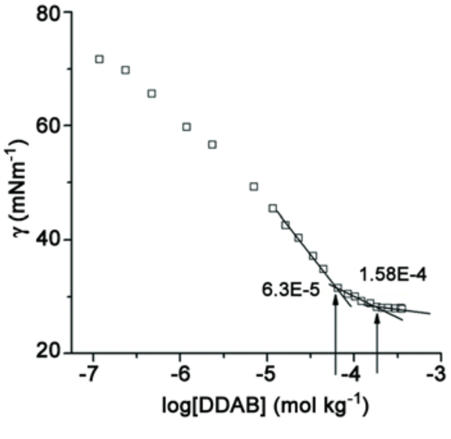

Fig. 1 — Surface tension isotherm of aqueous DDAB solution at 25 ºC.

DDAB in water, the first and second breaks in the surface tension isotherm have been ascribed to the formation of DDAB micelles and vesicles, respectively. Therefore, judging from the nature of surface tension curve of DDAB in water, the two breaks in the γ curve of DDAB in presence of NaBr might hint towards the formation of different nature of aggregates of DDAB. Adding NaBr gradually decreases the concentration value of the first and the second transition points and from [NaBr] = 10 mmol kg^{-1}

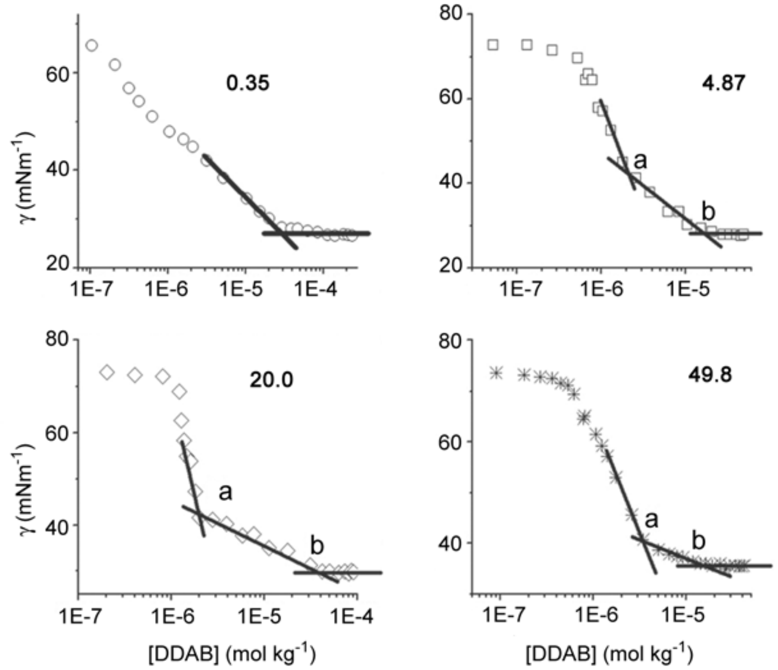

Fig. 2 — Surface tension plots of DDAB + NaBr + water system at 25 ºC as a function of DDAB concentration. [Concentrations of NaBr in mmol kg^{-1} are indicated in the plots].

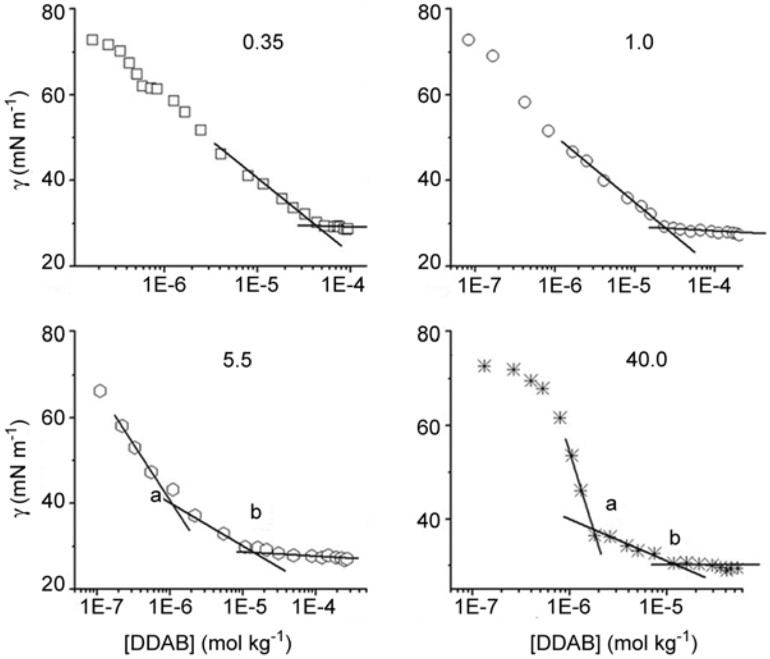

Fig. 3 — Surface tension plots of DDAB + NaCl + water system at 25 ºC as a function of DDAB concentration. [Concentrations of NaCl in mmol kg^{-1} are indicated in the plots].

onwards the effect is not pronounced and the concentration value at the first and second breaks remain unaffected (Table 1).

DDAB-NaCl and DDAB-NaB

In the case of added NaCl, DDAB displays normal surface tension curve with only one prominent break point at low concentrations, viz., 0.35 and 1.0 mmol kg^{-1} of NaCl (Fig. 3). The breaks in the γ curve at these two concentrations occur at *ca.* 0.05 and 0.03 mmol kg^{-1}, respectively, which are in consistent with the higher break point obtained in the case of added NaBr. When the added NaCl concentration is higher than 5.0 mmol kg^{-1} the γ curve shows two break points similar to aqueous NaBr (Fig. 3).The difference in the concentration between the first and second breaks is approximately 10-fold (Table 1).

In presence of added NaBz also, the variation of γ with [DDAB] shows double inflections (Fig. 4) similar to that in aqueous medium in the absence and presence of NaBr and NaCl. The concentration values corresponding to the first and second break points gradually decrease with increase in [NaBz] up to 1.0 m*M* of added NaBz (Table 1). The concentration values at the first and second break points in the γ isotherm have been discussed in detail in the preceding section.

Thus, it is clear from the surface tension plots that DDAB displays in aqueous medium two types of surface tension profile (X and Y as shown in Fig. 5) in the presence of salts as shown in Figs 2–4. The curve X is a typical behavior of normal micelle forming systems. In curve Y, surface tension decreases rapidly up to the first inflection point at ‘a’, then gradually goes down to the point ‘b’, and becomes constant thereafter. The slow decrease of γ in the region between ‘a’ and ‘b’ in Fig. 5 indicates the formation of pre-micellar aggregates composed of a very small number of DDAB molecules. According to thermodynamic consideration on adsorption from small aggregate solutions[33], the ratio $\partial\gamma/\partial \log c$ just below and above the inflection point approximately gives an average aggregation number by

$$N = (\partial\gamma/\partial \log c)_{c<\mathrm{cmc}}/(\partial\gamma/\partial \log c)_{c>\mathrm{cmc}}$$

Under the assumptions that distribution of aggregation number is very small and the adsorption does not change after the cmc, N is found to be ~5-8 for all the curves which followed surface tension change as depicted in Fig. 5 for the curve Y. Thus, transition points in the surface tension of DDAB in aqueous salt solution are mainly due to the formation of DDAB aggregates composed of different aggregation numbers. Grillo *et al.*[34] reported similar surface tension behavior of DDAB/tetraethylene glycol monododecyl ether mixture and showed on the basis of small angle neutron scattering (SANS) experiment that the two distinct breaks in the surface tension isotherms correspond to different kinds of aggregates (micelles and vesicles). Given the fact that the packing parameter of DDAB is close to unity, the formation of spherical micelles at the break point in

Table 1 — Value of cmc of DDAB in aqueous electrolyte medium at 25 ºC (cmc±0.0001 mmol kg^{-1})

[Salt] (mmol kg^{-1})	Surface tension		Fluorescence	Conductance
	a	b		
		NaBr		
0.35		0.0275	0.0362	0.0323
0.75				0.0211
1.76	0.0156	0.0295	0.0202	0.0199
4.87	0.0019	0.0174	0.0077	
9.4	0.0030	0.0234	0.0106	
15.4	0.0030	0.0199	0.0075	
20.0	0.0021	0.0234	0.0102	
30.0	0.0025	0.0195	0.0077	
40.0	0.0036	0.0168		
50.0	0.0040	0.0141	0.0038	
		NaCl		
0.35		0.0483	0.0485	0.0405
0.75		0.0370	0.0390	0.0316
1.1		0.0276	0.0332	0.0253
5.5		0.0105	0.0196	0.0098
10.0	0.0014	0.0091	0.0205	
14.9	0.0024	0.0120	0.0195	
19.8	0.0021	0.0191	0.0147	
30.0	0.0020	0.0224		
40.0	0.0017	0.0120	0.0076	
		NaBz		
0.05		0.0355		
0.08		0.0282		0.0348
0.3	0.0025	0.0121		0.0165
0.8	0.0011	0.0050	0.0143	0.0060
1.0	0.0017	0.0199		
5.0	0.0027	0.0129	0.0095	
10.0	0.0017	0.0092	0.0055	
20.0	0.0027	0.0147		
39.4	0.0047	0.0240	0.0116	
51.3	0.0020	0.0158		

The column ‘a’ and ‘b’ represents the lower and the higher breaks in the surface tension isotherms of DDAB.

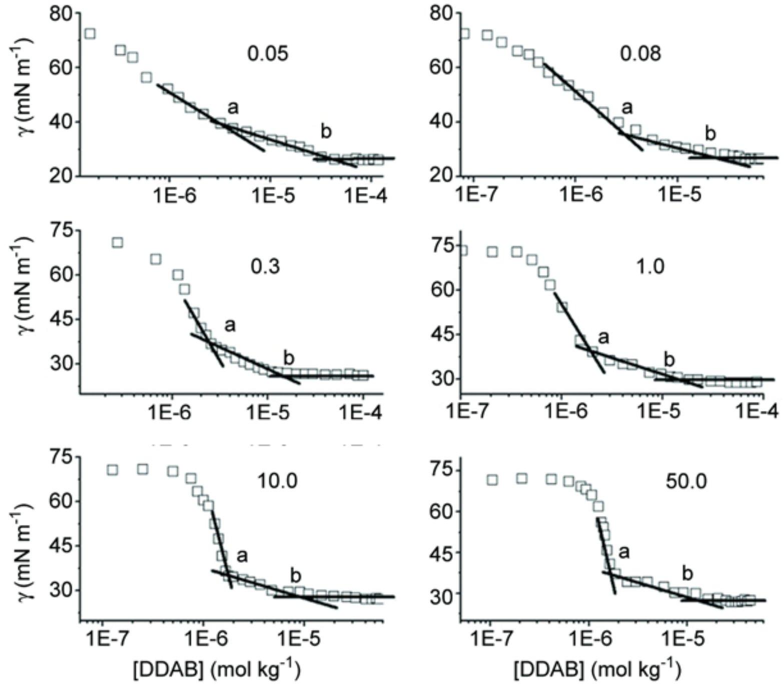

Fig. 4 — Surface tension plots of DDAB + NaBz + water system at 25 ºC as a function of DDAB concentration. [Concentrations of NaBz in mmol kg^{-1} are indicated in the plots].

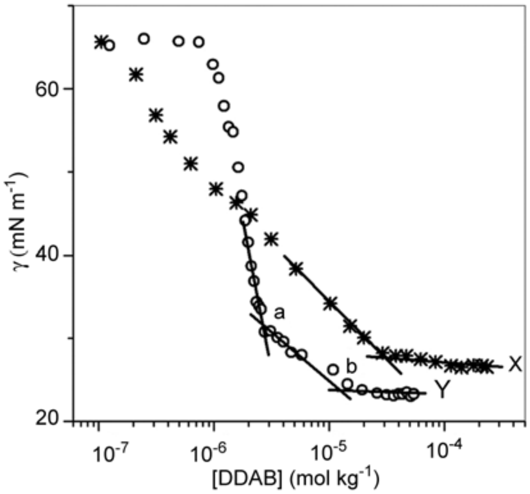

Fig. 5 — Surface tension versus concentration curves of the representatives of two types. The curve of type Y is shifted downward by 5 mN m^{-1} to obtain clarity on the transition

the surface tension curve is rather unfavorable. Marques *et al.*[27] investigated the nature of self-assembly of DDAB in water by NMR self-diffusion measurements and pointed out that DDAB self-assembles into micelles in a very narrow concentration range and also indicated co-existence of micelles and vesicles when the concentration (*c*) lies in the range [0.15 wt% (0.0032 m*M*) < *c* < (≈ 0.05 m*M*) cmc]. SANS measurements using a very high flux spectrometer such as D22 demonstrated the formation of small micelles and thus confirming the existence of a true cmc in the DDAB/D_2O system as showed by Marques *et al.*[27] The existence of two breaks in the surface tension isotherm is also reported in several other mixed systems containing DDAB as discussed above. Such adsorption behavior reflected in the surface tension isotherm is frequently obtained in the presence of DDAB which suggests that it is strongly linked to the particular nature of DDAB molecules.

It is quite pertinent to mention here that in the reported mixed systems[28,30-33] the breaks in the ST isotherm of DDAB corresponding to cmc and cvc (critical vesicle concentration) occurred at relatively higher concentrations, i.e., around 10^{-4} and 10^{-3} mol kg^{-1}, respectively. In the present study, the inflection points in the γ curve of DDAB in aqueous salt media occur around 10^{-6} mol kg^{-1} to 10^{-5} mol kg^{-1}. The concentrations corresponding to the lower (near point ‘a’ in Fig. 5) and higher (near point ‘b’ in Fig. 5) inflection points are listed in Table 1. Due to the presence of more than one inflection points in the γ curves of DDAB in presence of added salt, it is necessary to verify the values of the critical aggregation concentrations of DDAB obtained by surface tension technique using other complementary

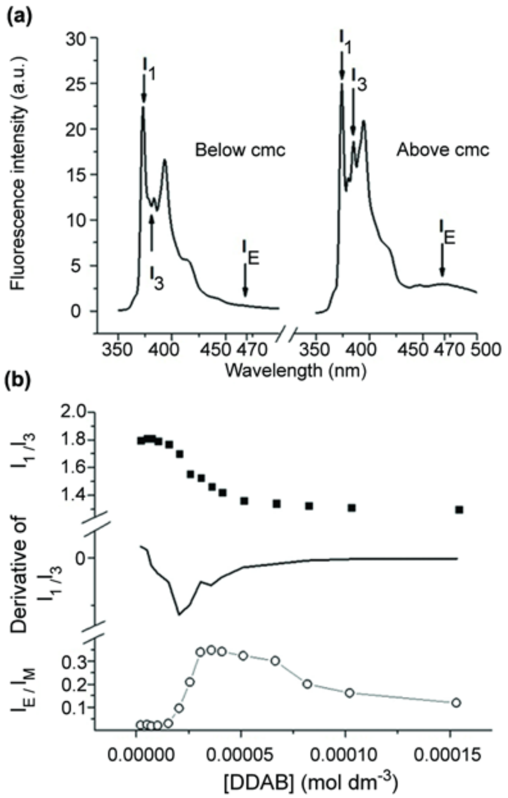

Fig. 6 — (a) Fluorescence emission spectra of pyrene in a surfactant solution with the band intensities used in the study, and, (b) spectral ratios I_E/I_M (○), I_1/I_3 (□) and its derivative (solid curve).

techniques like conductance and pyrene fluorescence emission method.

Fluorescence

We made an attempt to study the aggregation behavior of DDAB from the fluorescence intensity ratio of pyrene molecule. Figure 6 shows the characteristic fluorescence emission spectrum of pyrene below and above cmc of a surfactant. The emission spectrum of pyrene monomer shows five maxima in the region 370-400 nm along with an excimer peak at 470-475 nm. The critical micelle concentration (cmc) is determined here from the pyrene emission spectra by I_1/I_3 (I_1 and I_3 are the intensity of the first and the third peak respectively) and I_E/I_M (I_E and I_M are the intensity of the excimer and monomer bands, respectively) methods. In one method, derivative plots (solid curve in Fig. 6, lower panel) were drawn and DDAB concentration corresponding to deep minimum in the derivative plot was noted down and compared with the inflection points in the γ curve. For all the cases the minimum in the derivative plot corresponds to the higher break point in the γ curve. In the second method, the intensity ratio of the monomer emission band (373 or 383 nm) to the excimer emission band (470 nm) was used to locate the cmc of DDAB. The I_E/I_M ratio of pyrene increases initially and then decreases; the maximum peak position is taken as the cmc.[35, 36] In this method too, the peak maximum of I_E/I_M ratio of pyrene agrees more with the higher inflection point in the γ curve. The cmc values obtained from these two methods are very close to each other and thus we decided to take a common value obtained from these methods, which are listed in the Table 1. Although less used, the I_E/I_M method can be used more often in surfactant systems to locate the cmc owing to its easy applicability in comparison to the I_1/I_3 plot where model fittings are required to determine cmc.

Conductance

The specific conductance (κ) values of DDAB in water as a function of [DDAB] is shown in Fig. S1 (Supplementary Data). The break in the conductance curve occurs at 0.178 mmol kg^{-1} of [DDAB] and is close to the higher inflection point in the γ curve, viz., 0.158 mmol kg^{-1} (refer to Fig. S1). Thus, conductance method could not detect the lower concentration break point, *ca*. 0.063 mmol kg^{-1} as detected by the surface tension technique. The representative κ versus [DDAB] plots in aqueous NaBr, NaCl and NaBz media are given in Figs S2–S4 (Supplementary Data) and the concentrations of DDAB at the break point are given in Table 1. The conductance method has some limitation in locating the cmc at high concentration of the salt as the variation of the κ with DDAB concentration is not so significant beyond some concentration of the salt and hence data are not taken into account. Thus, both fluorescence and conductance methods unlike surface tension supports only one break point which corresponds to the higher value of the break point obtained from γ curve.

Of the three methods used for determination of cmc of DDAB, surface tension method highlights the existence of two breaks in the surface tension isotherm. The cmc obtained from fluorescence and conductance methods supports only the higher break point obtained in the surface tension isotherm. Only in the cmc values obtained from these three methods are in reasonable agreement.

Critical micelle concentration (cmc) and its dependence on counterion

The two reported values of cmc of DDAB in water[24-28] are around 0.063 mmol kg^{-1} and 0.158 mmol kg^{-1}. The

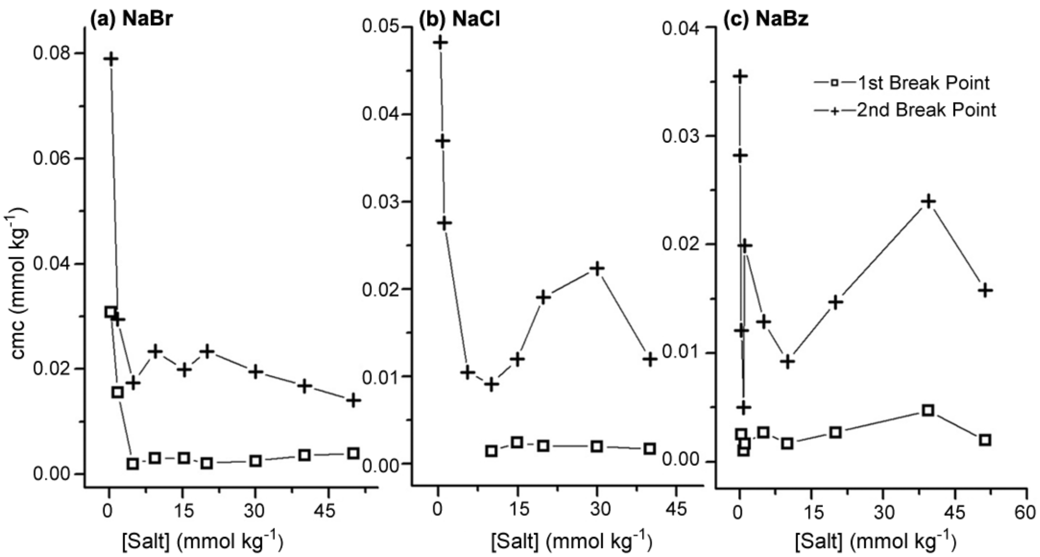

Fig. 7 — Change in cmc of DDAB (at 25 ºC) in presence of (a) NaBr, (b) NaCl and (c) NaBz. [The values are obtained using surface tension measurements].

cmc of DDAB in aqueous medium determined from surface tension also revealed two break points in close proximity to the above mentioned reported values of cmc as shown in Fig. 1. The cmc values of DDAB in aqueous medium in presence of different salts determined from surface tension isotherms are listed in Table 1 and also shown in Fig. 7. For comparison, the cmc determined using fluorescence and conductance methods are also listed in Table 1. The lower break point marked as ‘a’ has weak dependence on the concentration of added counterion and do not follow a regular trend in the variation of cmc upon adding an electrolyte. It is quite obvious because at the point ‘a’, DDAB only forms small aggregates as discussed in the preceding section. Thus, the present study clearly shows that the higher inflection point marked as ‘b’ in the surface tension isotherm is the true cmc value of DDAB and therefore it is not correct to identify DDAB to have two cmc values. At a particular concentration of the added salt, cmc values follow the order: NaBz < NaBr < NaCl. Usually, a continuous decrease in the cmc of a surfactant with increase in the salt concentration and then saturation at higher concentration of the salt is observed. In the present case, the salt affects the cmc of DDAB only in a narrow range of very low concentration of the added salt. For instance, in the case of added NaBr (0.35 m*M*), the cmc of DDAB decreased from 0.158 mmol kg^{-1} (in absence of salt) to 0.029 mmol kg^{-1}. Further increase in concentration of added NaBr had negligible effect on the aggregation property of DDAB as shown in Fig. 7. Similar observations were made in the case of NaCl and NaBz also (Fig. 7). Thus, from Fig. 7, we can infer that only low concentration of a salt has significant effect on the aggregation property of DDAB which is quite unusual from the normal behavior of other ionic surfactants like sodium dodecylsulphate (SDS) and cetylpyidinium chloride (CPC) wherein effect of salt on the respective cmc values is noticed up to quite high salt concentrations.

Counterion binding behavior

The counterion binding constant (β) of an ionic surfactant is commonly determined by using the Corrin-Harkins (CH) equation[17],

$$\ln c_0 = \mathrm{A} - \beta \ln(c_0 + c_e) \quad \ldots (1)$$

where A is a constant related to the free energy of micellization and c_0 and c_e represent the cmc and electrolyte concentration respectively. The sum ($c_0 + c_e$) is equal to the total concentration of the free counterions in the solution at cmc. Equation (1) was derived for the case of ionic surfactant solutions in the presence of added 1:1 electrolyte containing the same counterion as that of the surfactant. Recently, we showed that when the ionic surfactant and the added electrolyte contain different counterions i.e., for mixed counterion systems, CH equation takes a modified form as shown in the following expression[18],

$$\ln c_0 = \mathrm{A'} - \mathrm{B} \ln c_e \quad \ldots (2)$$

where A' = $\Delta G_{\mathrm{m}}^{0}/[(1+\beta_1)RT]$ and B = $\beta_2/(1+\beta_1)$. $\Delta G_{\mathrm{m}}^{0}$ is the standard energy of micellization per mole of ionic surfactant, and, β_1 and β_2 are the counterion binding constants of the counterions 1 (counterion from the surfactant) and 2 (counterion from the added electrolyte), respectively. The total counterion binding constant β is given by $\beta_1 + \beta_2$. When $c_e = 0$, B also tends to zero and Eq. (2) becomes $\ln c_0 = A'$, which gives the well known expression for the standard free energy of micellization of ionic surfactant. However, the modified form of the CH equation, unlike the CH equation, does not give the value of β directly from the slope. The applicability of the CH equation[17] is also reported to be limited in the case of ethylene glycol-water medium.[37]

DDAB/NaBr system

The cmc of DDAB in H_2O is 0.158 mmol kg^{-1} and the decrease in the value of cmc of DDAB in the presence of salt reaches a saturation value (no further decrease in the cmc) at a very low concentration of the added salt as already mentioned above. In general, the cmc values of common ionic surfactants are known to follow CH relation in the electrolyte concentration range up to 0.1 to 0.2 *M* for univalent salts. In the electrolyte concentration range typically of the order of 0.3 *M* or higher, the deviation from the linearity in the CH plot occurs owing to the salting-out effect or shape change of the micellar aggregate. In the present case however, beyond 10 mmol kg^{-1} of added NaBr, linearity in the CH plot disappears (Fig. 8). Thus, we have not considered the cmc values of DDAB beyond 10 mmol kg^{-1} of added salt (data inside the square box in Fig. 8a) for employing CH relation. The CH plot of DDAB in presence of added NaBr is shown in Fig. 8b. It shows a single region of counterion binding constant and the value of β is estimated to be 0.52. Reportedly, the values of β for DDAB in H_2O (in absence of added salt) were estimated to be 0.26 (DDAB= 0.05 m*M*)[38] and 0.35 (DDAB=0.07 m*M*)[39] using ion selective electrode. Thus, the obtained β value of DDAB in presence of NaBr near the cmc region shows almost a 50% increase in the counterion binding constant value when compared with the reported value, which is certainly due to the binding of bromide ions from added salt.

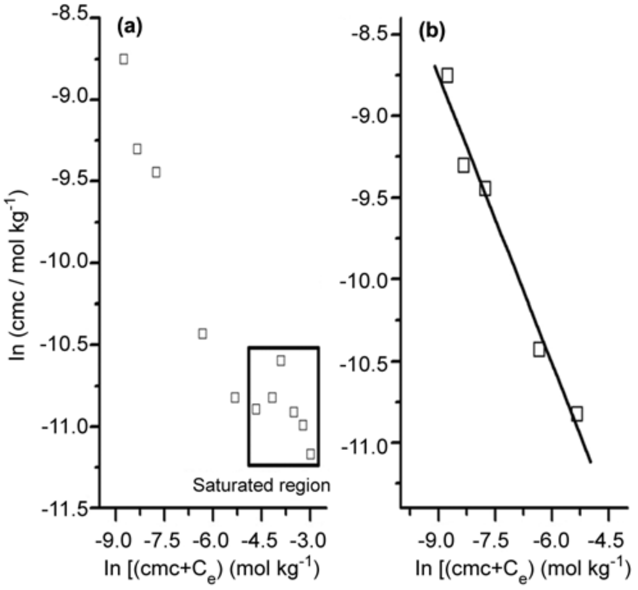

Fig. 8 — (a) C-H plot for DDAB in aqueous NaBr showing the saturated data inside the square box, and (b) CH plot and linear fitting to the data excluding the data inside the square box.

DDAB/NaCl system

DDAB-NaCl system contains mixed counterions, viz., Br$^-$ and Cl$^-$ and hence theoretically the CH equation is not applicable to such a system. From Fig. 9a, it is clear that the deviation occurs in presence of added NaCl also, however we found that the deviation from the CH relation has still negative slope value which is consistent with the sign of the slope for C-H equation. Presence of mixed counterions is responsible for this deviation. Applying modified form of CH equation for data consisting of concentration of NaCl and corresponding cmc value of DDAB, we obtain linear plot (Fig. 9b) which

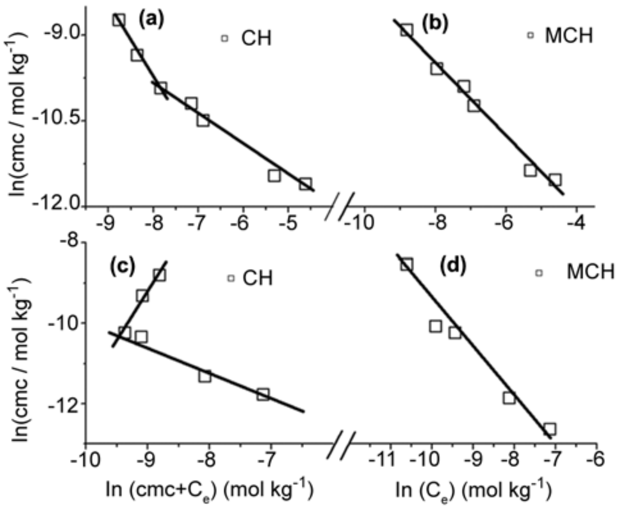

Fig. 9 — (a) C-H and (b) modified C-H plots of DDAB in aqueous NaCl, and, (c) CH and (d) modified CH plots of DDAB in aqueous NaBz.

proves the applicability of modified CH equation to mixed counterions in aqueous surfactant solution. By least squares fitting of the data shown in Fig. 9b, we obtained B = 0.54 which is nearly equal to the slope value (~0.56) of CH plot in the higher concentration range.

DDAB/NaBz system

The DDAB-NaBz system also contains mixed counterions, viz., Br^- and added benzoate ions. The variation of cmc of DDAB with added NaBz is not significant beyond 0.8 mmol kg^{-1} and hence the data beyond this concentration is not taken into consideration (Fig. 9c). Unlike in the case of added NaCl, the deviation in the CH plot (Fig. 9c) for DDAB at low concentration of added NaBz is more drastic with a reversal in the sign of the slope from negative to positive which highlights the limitation of CH to mixed counterion solutions. In Fig. 9d, we have shown the plot for ln cmc versus ln c_e and the linearity of the plot envisages the applicability of modified CH equation instead of CH equation. By least squares fit of the data (Fig. 9d), we obtain the value of B equal to 0.59. In the case of mixed counterions, the slope B of the modified CH plot does not correspond to β but provides lower limit to the value of β. Thus, β must be more than 0.59.

Dynamic light scattering measurements

The aqueous solutions of DDAB in presence of salt (NaBr, NaCl, NaBz) show two transition points marked as ‘a’ and ‘b’ in the surface tension plots. Fluorescence and conductance measurements could only sense the higher transition point (‘b’). In order to identify the nature of these aggregates we carried out the DLS measurements. However DLS showed no detectable intensities in both the concentration regions due to very low concentrations of DDAB aggregates near or at cmc. DLS studies may not be optimum to scatter enough light for measurement at very low concentrations. Thus, the size effects of added counterions towards the DDAB aggregates have not been successfully determined using DLS studies at cmc. However, it would be worthwhile to study the effect of added counterion on the size of surfactant aggregates by taking a higher range of surfactant concentration than the cmc.[40] Therefore, to study the role of added counterions on DDAB aggregates, we kept the concentration of DDAB fixed ([DDAB] = 0.5 mmol kg^{-1}) and varied the concentration and type of added counterion. Figure 10 shows the variation of the size of DDAB with increasing amount of salt.

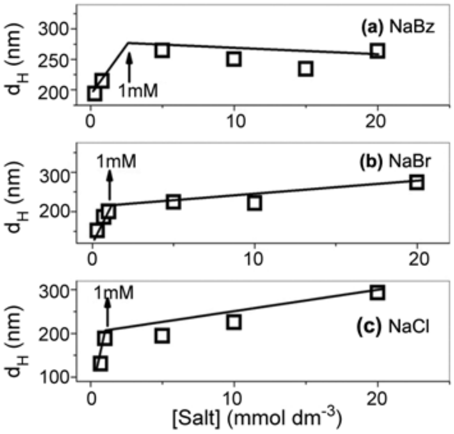

Fig. 10 — Variation of size of DDAB aggregate (conc. of DDAB = 0.5 m*M*) with increasing concentration of salt. [(a) NaBz; (b) NaBr; (c) NaCl].

The variation in the size of the DDAB aggregate follows the order: NaBz > NaBr > NaCl. On adding salt, the value of d_H increases and reaches almost saturation value at very low concentration of the added salt equal to 1 mmol kg^{-1}. Since it has been reported in the literature that for a binary DDAB–water system, vesicular aggregates can be formed at very low concentration range of DDAB[41], therefore, from the obtained values of the hydrodynamic radii of the DDAB aggregate (which is more than 200 nm), it is quite certain that DDAB molecules adopt vesicular aggregate structure in presence of these salts. The higher values of the hydrodynamic radii obtained in the case of NaBz can be attributed to both the electrostatic and hydrophobic binding of the benzoate counterions. Thus, with respect to both size and cmc, higher concentrations of added counterions seem to have very little effect on DDAB.

Conclusions

The effect of counterions on the solution behavior of DDAB has been studied using surface tension, fluorescence, conductance and dynamic light scattering methods. The first noteworthy observation of this system is the presence of two break points in the surface tension profile in aqueous electrolyte solution. The first break point in the surface tension curve is possibly due to the pre-micellar aggregates composed of a very small number of DDAB molecules. The higher break point in the surface tension curve is the true cmc of DDAB supported by all the techniques employed for the present study. The effect of the counterions on the aggregation behavior of DDAB is significant only at very low concentration of the counterions. In agreement to our previous studies[18], the Corrin-Harkins equation normally used to study counterion binding behavior of ionic surfactants in presence of counterions fails in the case of mixed counterions. The modified Corrin-Harkins[18] equation successfully explains the counterion binding behavior of DDAB in the presence of added chloride and benzoate mixed counterions. The determined degree of counterion binding onto the DDAB aggregates is found to be greater than 60%, which indicates a good aggregate stability.

Supplementary Data

Supplementary data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_56A(11)1122-1131_SupplData.pdf.

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