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ORIGINAL CONTRIBUTION

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Surfactant polymer interactions between strongly interacting cationic surfactants and anionic polyelectrolytes from conductivity and turbidity measurements

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Abstract The interactions between oppositely charged surfactant/polymer mixtures have been studied using conductivity and turbidity measurements. The dependence of aggregation phenomenon on the chain length and head group modifications of conventional cationic surfactants, i.e., hexadecyl- (HTAB), tetradecyl- (TTAB), and dodecyltrimethylammonium bromides (DTAB) and dimeric cationic surfactants, i.e., decyl- (DeDGB) and dodecyldimethylgemini bromides (DDGB), is investigated. It was observed that cationic surfactants induce cooperative binding with anionic polyelectrolytes at critical aggregation concentration (cac). The cac values are considerably lower than the critical micelle concentration (cmc) values for the same surfactant. After the complete complexation, free micelles are formed at the apparent critical micelle concentration (acmc), which is slightly higher in aqueous polyelectrolyte than in pure water. Among the conventional and dimeric cationic surfactants, DTAB and DeDGB, respectively, have been found to have least interactions with oppositely charged polyelectrolytes.

Keywords Cationic surfactants · Anionic polyelectrolytes · Dimeric gemini · Conductivity · Turbidity

Introduction

Interactions between a polyelectrolyte and surfactant in aqueous solutions have been investigated for several decades and are extensively documented [1, 2]. In particular, there have been significant research efforts focusing on polyelectrolyte oppositely charged surfactant interactions in recent years [3, 4, 5, 6, 7, 8, 9, 10, 11, 12]. Indeed such studies can be applied to a large number of industrial as well as biological processes. The association between the polymers and surfactants has been largely rationalized as a consequence of hydrophobic and electrostatic interactions [13, 14]. While interactions between non-ionic polymers and ionic surfactants rely mainly on hydrophobicity [1, 2], attractive electrostatic forces dominate in the case of polyelectrolytes and oppositely charged surfactants. In the presence of an oppositely charged polyelectrolyte, surfactant starts to form aggregates with polyelectrolyte as the surfactant concentration exceeds a critical value referred as critical aggregation concentration (cac). In this process, the counter ion of the polyelectrolyte is replaced by the surfactant ion, and the binding site of the polyelectrolyte and the surfactant form a neutral ion pair. The large electrostatic attraction in this association process makes binding extremely favorable as well as dependent on the ionic charge density of the polymer. Binding in these systems therefore occurs at very low free surfactant concentration, often one to three orders of magnitude below the cmc of the surfactant. This is a cooperative process, which can be considered analogous to the spontaneous association of surfactant monomers in aqueous solution in the absence of polyelectrolyte [15], which takes place within a narrow concentration interval when the surfactant concentration exceeds the cmc.

The experimental efforts in this field were first devoted to the determination of binding isotherms [6, 7, 8], enthalpies of binding [9], and various thermodynamic and transport properties [10] in solutions of polyelectrolytes with added surfactants. Hugerth et al. [16] have studied the effect of polyelectrolyte counter ion specificity on dextran sulphate–amphiphile interactions in water and aqueous/organic solvent mixtures. The results indicated a close correlation between the ion specificity of polyelectrolyte, and the effect of different counterions on polyelectrolyte–amphiphile interaction. Kogej et al. [17] studied the micelle formation of alkyltrimethylammonium surfactants in aqueous PSS solutions by fluorescence and conductivity measurements. The dependence of aggregation phenomenon on the chain length of surfactant and on the ionic strength of the solution was investigated.

These interactions can be well quantified by choosing ionic surfactants of different head group architectures in combination with oppositely charged polyelectrolytes. To achieve our goal, we have chosen three conventional cationic surfactants (HTAB, TTAB, and DTAB) and two cationic geminis (DDGB and DeDGB). Four anionic polyelectrolytes have been selected for this study and are carboxymethyl cellulose sodium salt (CMC), dextransulfate sodium salt (DX), poly(styrene sulfonate) sodium salt (PSS), and poly(acrylic acid) sodium salt (PAA). The strength of interactions between oppositely charged surfactant–polyelectrolyte components have been studied by head group and hydrophobic tail modifications by comparing the behavior of conventional single tail cationic with double tail dimeric gemini surfactants.

Experimental section

Materials

HTAB, TTAB, and DTAB from Lancaster Synthesis, UK, were used as received. Cationic geminis, DDGB and DeDGB, were synthesized according to the method reported elsewhere [18]. CMC (av. mol. wt. 100,000), DX (av. mol. wt. 500,000), PSS (av. mol. wt. 70,000), and PAA (av. mol. wt. 30,000) obtained from TCI, Japan, were used as received. Distilled conductivity water was used in the preparation of all solutions. The solutions were prepared by mass with an accuracy of 0.01 mg. All the measurements were performed at 25 °C after giving sufficient time for stabilization.

Conductivity measurements

The conductivity (κ) measurements of surfactants in the absence as well as in the presence of different polyelectrolytes were carried out with the help of digital conductivity meter model EQ 661. A dip-type conductivity cell with a double-walled jacket to circulate the thermostated water was used for all the measurements. An automatic thermostat bath from Julabo F25, Germany, was used for maintaining the temperature within the uncertainties of ±0.05 °C. Titrations were performed by adding concentrated stock solution of each surfactant in aqueous polyelectrolyte reference solution, keeping the concentration of polyelectrolyte constant.

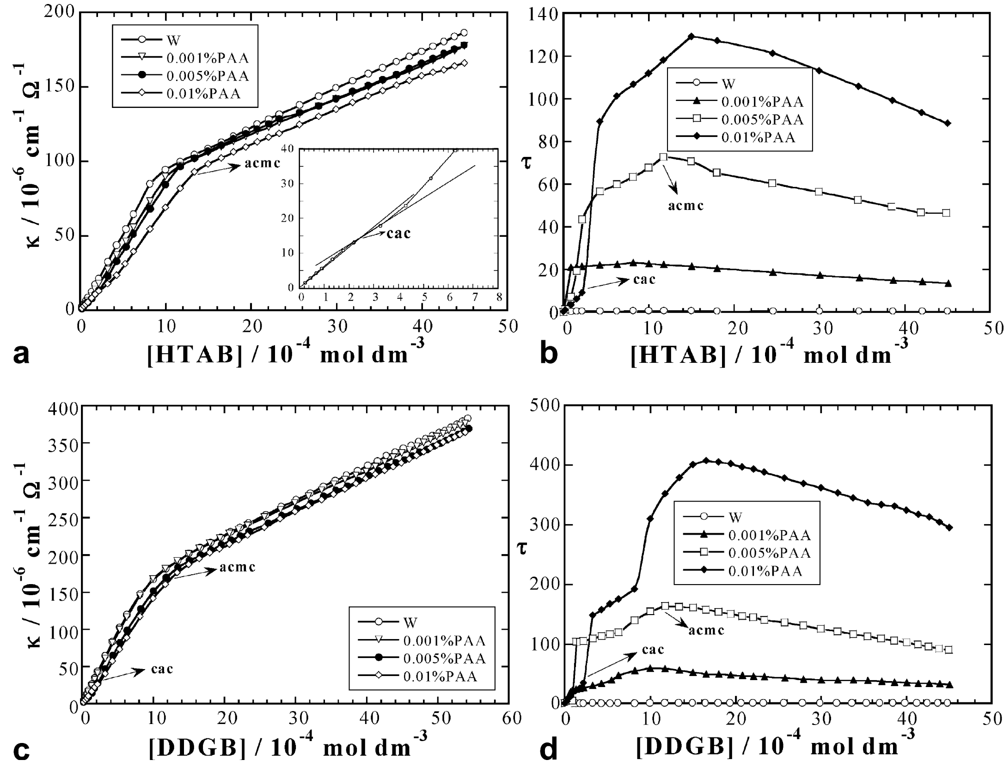
Turbidity measurements

The turbidity measurements of the same systems were carried out using a Nephelo-Turbidity meter model CL 52D after allowing sufficient time for equilibration. This instrument works on the basis of scattering of light by the colloidal particles. The light coming from the light source is focused in the colloidal solution by passing it through a pair of lenses and the scattered light at a right angle to the incident light is detected by a photo multiplier tube, which gives the turbidity of the solution in arbitrary nephelo turbidity units.

Results and discussion

Polyelectrolyte–surfactant interactions are characterized by cooperative binding of surfactant with oppositely charged polyelectrolyte and by distinct changes at one or two critical surfactant concentrations. Collective representative κ plots of HTAB + PAA + water(W) and DDGB + PAA + W systems are shown in Fig. 1. Similar plots were observed for other combinations. The addition of HTAB in pure water caused a linear increase of κ up to the surfactant concentration at which micelles began to form, i.e., up to cmc. After the cmc, κ increased further, but with a smaller slope than before the cmc. The break on the conductivity-concentration titration curve gives the cmc of surfactant by linear fitting the data in the pre- and the post-micellar regions [19, 20]. On the addition of HTAB to aqueous 0.01% PAA solution, due to the electrostatic interactions, the surfactant monomers may bound ionically to the accessible binding sites on the surface of the polyelectrolyte molecule, forming a surfactant-polyelectrolyte complex. This concentration of the surfactant is referred to as cac (Fig. 1a, inset), which is two to three orders lower than the actual cmc in pure water. However, further increase in the surfactant concentration leads to another break, which is close to the cmc value in pure water. This latter break is known as apparent critical micelle concentration (acmc). Only single transition (i.e., acmc) is observed at lower polyelectrolyte concentrations, i.e., 0.001% and 0.005% PAA, while at higher 0.01%, both cac and acmc are observed. Similarly, both transitions are observed for DDGB in aqueous 0.01 and 0.005% PAA in Fig. 1c. The cac indicates the saturation of charged sites of polyelectrolyte by surfactant monomers and acmc shows the formation of independent micelles thereafter. The cac, acmc, and cmc values from κ studies for the present surfactants in aqueous CMC, DX, PSS, and PAA have been listed in Table 1. The acmc values

Fig. 1 a Conductivity, κ, versus total concentration of HTAB in the absence and in the presence of various concentrations of PAA. *Inset*: enlarged view at 0.01% PAA showing cac. **b** Turbidity, τ, versus total concentration of HTAB in the absence and in the presence of various concentrations of PAA. **c** Conductivity, κ, versus total concentration of DDGB in the absence and in the presence of various concentrations of PAA. **d** Turbidity,τ, versus total concentration of DDGB in the absence and in the presence of various concentrations of PAA



obtained are always higher than the cmc in pure water. This indicates the micelle formation in the presence of polyelectrolytes is taking place at higher surfactant concentration due to the formation of surfactant-polyelectrolyte complex, which reduces the actual amount of surfactant available for independent micellization.

Apart from this, τ measurements are more sensitive than κ as far as the interactions between the oppositely charged surfactants and polyelectrolytes are concerned. Figures 1b and d show the τ of HTAB and DDGB in the presence as well as in the absence of PAA. Similar plots were observed for other systems. A distinct break at low surfactant concentration at all polyelectrolyte concentrations represents the cac. This break signaled the initiation of interaction between the surfactant and polyelectrolyte. Electrostatic interactions between cationic surfactants and the anionic polyelectrolytes lead to the insoluble salt formation, which is indicated by instant increase in the τ value. At a certain point, an instant increase in τ value turns to a gradual increase up to a maximum, giving rise to a two-step adsorption isotherm. This two-step curve is quite clear for both the geminis, i.e., DDGB (Fig. 1d) and DeDGB (see later). Therefore, the first step corresponding to instant increase in the τ value is related to the neutralization of oppositely charged electrical sites available both on the cationic surfactant head groups and anionic polyelectrolytes. While the second step of gradual increase in τ can be related to an adsorption process governed by hydrophobic sites of both surfactants and polyelectrolytes. Since dimeric surfactants possess double hydrophobic tails, the second step is quite prominent in the case of DDGB and DeDGB. A decrease in the τ value thereafter indicates the solubilization of insoluble salt in the micelles. The concentration of the surfactant where turbidity starts decreasing denotes the independent micelle formation process and is represented by acmc. The cmc, cac, and acmc values thus obtained for various systems from τ measurements have also been listed in Table 1.

Before discussing the various parameters of Table 1, it is desirable to discuss the turbidity behavior of HTAB, TTAB, and DTAB in aqueous CMC solutions. Figure 2 shows a comparison between the κ and τ plots. In the case of HTAB (Figs. 2a and b), a clear cac and acmc are observed from κ plot in 0.01% CMC but acmc is not visible from τ plots. Similar behavior is observed for TTAB (Figs. 2 c and d). In the case of DTAB, all the τ curves after the cac merge with that in pure water (Fig. 2f) and the concentration where it happens, is the same to that represented by acmc from the corresponding κ plot. The cac values in Figs. 2b and d have been taken before the respective maximum while in Fig. 2f the maximum itself has been taken as the cac. This difference is accounted for the insoluble salt for-

Table 1 Critical aggregation concentration (cac), critical micelle concentration (cmc), apparent critical micelle concentration (acmc), average acmc (acmc)$_{Av}$, and degree of binding (β) for various surfactants from conductivity (κ) and turbidity (τ) measurements in the presence of polyelectrolytes at 25 °C

Polymer	κ		τ		(acmc)$_{Av}$	β
	cac 10^{-4}mol dm^{-3}	cmc or acmc 10^{-4}mol dm^{-3}	cac 10^{-4}mol dm^{-3}	cmc or acmc 10^{-4}mol dm^{-3}		
HTAB + polyelectrolytes						
Water		9.1 ± 0.1				
0.001% CMC		9.3 ± 0.1	0.9		9.3	0.9
0.005% CMC		11.1 ± 0.2	2.2		11.1	1.3
0.01% CMC	2.6 ± 0.3	13.7 ± 0.3	2.8		13.7	1.5
0.001% DX		9.6 ± 0.1	0.9	9.5	9.5	0.8
0.005% DX		10.0 ± 0.3	2.2	10.0	10.0	0.3
0.01% DX		13.4 ± 0.3	2.2	13.4	13.4	0.7
0.001% PSS		11.7 ± 0.3	0.9	11.7	11.7	5.4
0.005% PSS		10.5 ± 0.1	2.2	11.0	10.7	0.7
0.01% PSS		11.9 ± 0.2	2.2	12.0	11.9	0.6
0.001% PAA		10.6 ± 0.1	0.9	10.5	10.6	1.4
0.005% PAA		11.5 ± 0.1	1.5	11.5	11.5	0.4
0.01% PAA	2.3 ± 0.2	13.7 ± 0.1	2.3	13.7	13.7	0.4
TTAB + polyelectrolytes						
Water		37.6 ± 0.3				
0.001% CMC		37.8 ± 0.3	5.0	37.8	37.8	0.6
0.005% CMC		39.6 ± 0.4	6.0	39.6	39.6	1.2
0.01% CMC		42.5 ± 0.5	7.0	42.5	42.5	1.6
0.001% DX		41.7 ± 0.1	0.9		41.7	6.7
0.005% DX		39.0 ± 0.2	2.1		39.0	0.4
0.01% DX		40.3 ± 0.5	2.2		40.3	0.4
0.001% PSS		39.0 ± 0.3	0.9	39.0	39.0	2.9
0.005% PSS		38.1 ± 0.3	2.0	38.0	38.0	0.2
0.01% PSS		39.9 ± 0.3	2.0	39.9	39.9	0.5
0.001% PAA		37.7 ± 0.3	0.9	38.0	37.9	0.3
0.005% PAA	3.3 ± 0.9	39.8 ± 0.3	3.7	40.0	39.9	0.4
0.01% PAA	4.6 ± 0.9	40.9 ± 0.5	5.0	42.0	41.4	0.4
DTAB + polyelectrolytes						
Water		153 ± 1.4				
0.001% CMC		158 ± 1.6			158	17
0.005% CMC		159 ± 1.4			159	3.9
0.01% CMC		158 ± 1.3			158	1.6
0.001% DX		156 ± 1.5	5.0	156	156	4.8
0.005% DX		157 ± 1.4	9.9	157	157	1.3
0.01% DX		161 ± 1.3	15	161	161	1.3
0.001% PSS		157 ± 1.4	15	157	157	7.4
0.005% PSS		162 ± 2.2	20	162	162	3.7
0.01% PSS		162 ± 1.8	25	162	162	1.9
0.001% PAA		153 ± 1.4	15	153	153	0.1
0.005% PAA		160 ± 2.0	20	160	160	1.3
0.01% PAA		161 ± 2.0		161	161	0.8
DDGB + polyelectrolytes						
Water		9.3 ± 0.1				
0.001%CMC		9.5 ± 0.1	0.6		9.5	0.6
0.005% CMC	0.9 ± 0.1	9.1 ± 0.2	0.9		9.1	0.1
0.01% CMC	1.2 ± 0.3	11.7 ± 0.4	1.3		11.7	0.8
0.001% DX		9.5 ± 0.1	0.6	9.2	9.3	0.1
0.005% DX		10.4 ± 0.1	0.9	10.4	10.4	0.4
0.01% DX		11.1 ± 0.3	2.1	11.1	11.1	0.3
0.001% PSS		9.8 ± 0.1	0.6	9.8	9.8	1.1
0.005% PSS		10.2 ± 0.2	0.9	10.2	10.2	0.3
0.01% PSS		11.6 ± 0.2		11.6	11.6	0.5
0.001% PAA		9.2 ± 0.1	0.6	9.2	9.2	0.1
0.005% PAA	1.0 ± 0.4	11.4 ± 0.4	1.0	11.4	11.4	0.4
0.01% PAA	3.1 ± 0.7	12.1 ± 2.6	3.0	12.1	12.1	0.3

Table 1 (Contd.)

Polymer	κ		τ		$(\text{acmc})_{\text{Av}}$	β
	cac 10^{-4}mol dm^{-3}	cmc or acmc 10^{-4}mol dm^{-3}	cac 10^{-4}mol dm^{-3}	cmc or acmc 10^{-4}mol dm^{-3}		
DeDGB + polyelectrolytes						
Water		69.9 ± 0.9				
0.001% CMC		70.1 ± 1.0	7.8	59.0		0.3
0.005% CMC		74.2 ± 1.0	12	108		2.7
0.01% CMC		74.7 ± 1.0	17	123		1.5
0.001% DX		70.1 ± 1.1	8.0	69.9	70.0	0.1
0.005% DX		71.6 ± 1.1	10	71.2	71.4	0.5
0.01% DX		75.9 ± 0.8	14	75.9	75.9	0.9
0.001% PSS		69.9 ± 0.6	8.0	69.9	69.9	0.0
0.005% PSS		72.3 ± 0.5	10	72.3	72.3	0.9
0.01% PSS		74.8 ± 0.8	12	74.8	74.8	1.0
0.001% PAA		71.4 ± 0.9	8.0			1.4
0.005% PAA		77.2 ± 0.7	10			1.3
0.01% PAA		79.0 ± 0.8	10			0.8

mation in the former cases which is relatively less soluble in the micellar phase, hence would overshadow the actual cac value. Therefore, the points shown by arrows in Figs. 2b and d actually corresponding to the cac values demonstrated by the corresponding κ plots (Figs. 2a and c, respectively), from which they also show an instantaneous increase in the τ value. It should be mentioned here that the maximum concentration covered in the case of each surfactant is roughly five times the cmc of that surfactant in pure water, i.e., 50, 200, and 800×10^{-4} mol dm^{-3} for HTAB, TTAB, and DTAB, respectively. This suggests that DTAB independent micelles (formed at acmc) are maximum capable of solubilizing the insoluble salt formed at the cac. It is also evident from the insignificant difference among the curves in the absence and presence of CMC (Fig. 2e). It is known that the increase in the hydrophobicity results in an increase in the micellar aggregation number (N_{agg}). The N_{agg} values for HTAB, TTAB, and DTAB in pure water are 60, 57, and 50, respectively [21]. A smallest N_{agg} for DTAB suggests higher polarity at the micelle-solution interface. A higher solubilization capacity of DTAB micelles can therefore be linked to this greater polarity. It means that DTAB-polyelectrolyte complex is not fully electrostatically neutralized due to relatively weaker association between DTAB and polyelectrolytes than that of TTAB and HTAB. Thus, this complex is more favorably solubilized in the micelles with stronger polarity at the micelle–solution interface. Hence, the DTAB-polyelectrolyte complex is fully solubilized in the DTAB micelles, whereas the complexes of TTAB and HTAB cannot fully solubilize in their respective pure micelles. Furthermore, if we compare the τ plots of Fig. 2 with those of DDGB and DeDGB in aqueous CMC (Fig. 3), one can see that clear acmc can be observed in both cases after the cac in Fig. 3. It means that acmc transitions are overshadowed by intense turbidity of insoluble salt formation at cac in the case of HTAB, TTAB, and DTAB while this is not so for DDGB and DeDGB. This indicates that stronger cooperative binding is demonstrated by former conventional surfactants than by latter gemini surfactants where steric hindrances seem to affect the electrostatic interactions.

A perusal of Table 1 suggests that the cac value for each surfactant increases significantly from 0.001 to 0.01% polyelectrolyte except in the case of TTAB and HTAB. In the latter cases, though there is a significant increase in the cac value from 0.001 to 0.005%, further increase in the amount of polyelectrolyte from 0.005 to 0.01% does not increase the cac appreciably. The increase in the cac value with the increase in the polyelectrolyte concentration is obviously related to the complexation of a greater amount of cationic surfactant. A further increase in the amount of polyelectrolyte from 0.005 to 0.01% may induce some kind of self aggregation in the polyelectrolyte macromolecule, with the result that cac remains constant. A relative comparison of all the cac values for HTAB, TTAB, and DTAB suggests that they are almost close enough to each other, especially in the case of TTAB and HTAB, while they are much higher in the case of DTAB. On the other hand, they are again much higher for DeDGB than DDGB, among the dimeric surfactants. A higher cac value can be related to the weaker association of that surfactant with polyelectrolyte [17].

It is also possible to evaluate the degree of binding (β) of cationic micelles to polyelectrolyte, which is given by the ratio of amount of surfactant bound [S_b] to the monomolar concentration of a polyelectrolyte [P_m] [1, 2]:

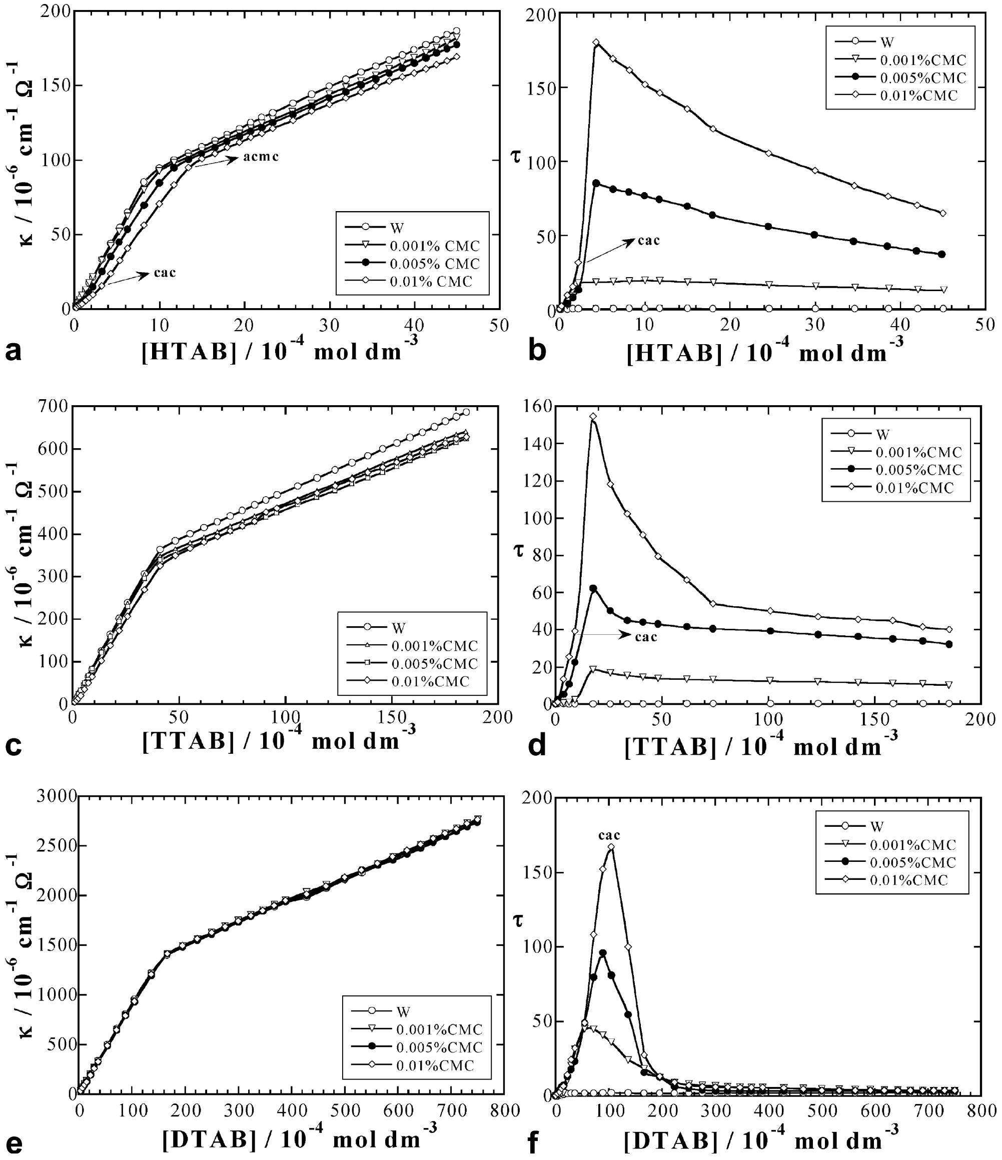


Fig. 2 a Conductivity, κ, versus total concentration of HTAB in the absence and in the presence of various concentrations of CMC. **b** Turbidity, τ, versus total concentration of HTAB in the absence and in the presence of various concentrations of CMC. **c** Conductivity, κ, versus total concentration of TTAB in the absence and in the presence of various concentrations of CMC. **d** Turbidity, τ, versus total concentration of TTAB in the absence and in the presence of various concentrations of CMC. **e** Conductivity, κ, versus total concentration of DTAB in the absence and in the presence of various concentrations of CMC. **f** Turbidity, τ, versus total concentration of DTAB in the absence and in the presence of various concentrations of CMC

$$\beta = [\mathrm{S_b}]/[\mathrm{P_m}] \qquad (1)$$

A difference between the $(\mathrm{acmc})_{\mathrm{Av}}$ and cmc would give the amount of a particular surfactant bound to the polyelectrolyte in view of their opposite polarities. Therefore, a non-availability of the amount of surfactant that has been complexed to polyelectrolyte would correspond to the difference between the acmc and cmc. β values thus computed have also been listed in Table 1. The β values for DeDGB + CMC systems were calculated only from κ data since acmc values from τ measurements were much higher due to some unknown reasons. These values for various surfactants are quite close to each other but mostly higher in the presence of 0.001% polyelectrolyte, whereas at higher concentrations they become very small. This is due to the fact that generally the difference between the cmc and acmc at 0.001% is much more significant since acmc hardly increases with the further increase in the amount of polyelectrolyte. A higher β value in aqueous 0.001% polyelectrolyte suggests the stronger association between a cationic surfactant and polyelectrolyte around this concentration, while further increase in the concentration of polyelectrolytes present does not enhance the degree of binding. Also, no systematic order is observed among the β values for various polyelectrolytes, and it seems that as if all polyelectrolytes have more or less equal magnitude of interactions with the surfactants present.

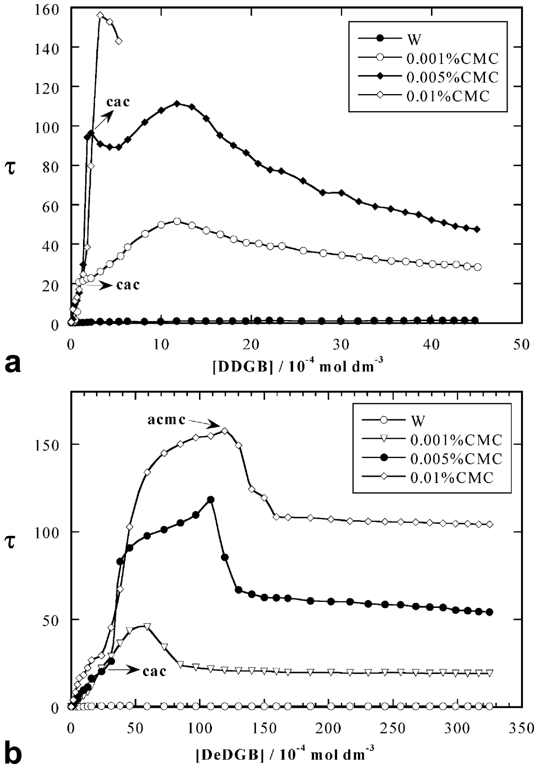


Fig. 3 a Turbidity, τ, versus total concentration of DDGB in the absence and in the presence of various concentrations of CMC. **b** Turbidity, τ, versus total concentration of DeDGB in the absence and in the presence of various concentrations of CMC

Conclusions

The conductivity measurements of conventional cationic HTAB, TTAB, and DTAB; and dimeric DDGB and DeDGB without and with the anionic polyelectrolytes (i.e., CMC, DX, PSS, and PAA) showed the existence of strong electrostatic interactions between the cationic surfactants and oppositely charged polyelectrolytes. The results obtained by turbidity measurements indicate a two-step adsorption isotherm in which the interactions start at a surfactant concentration referred as cac, which is much lower than the cmc of pure surfactant. At cac, the surfactant binds to the polymer due to strong electrostatic interactions and, after saturation of the binding sites of the polyelectrolyte, the surfactant concentration increases until it reaches the cmc of pure surfactant. The present study also shows that the interactions of DTAB and DeDGB with oppositely charged polyelectrolytes are comparatively weaker than those of the other conventional and dimeric cationic surfactants.

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