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ORIGINAL CONTRIBUTION

Mandeep Singh Bakshi
Ishpinder Kaur

Benzylic and pyridinium head groups controlled surfactant-polymer aggregates of mixed cationic micelles and anionic polyelectrolytes

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M.S. Bakshi (✉) · I. Kaur
Department of Chemistry,
Guru Nanak Dev University,
143005 Amritsar, Punjab, India
E-mail: ms_bakshi@yahoo.com

Abstract The oppositely charged electrostatic interactions between cationic single and mixed micelles of benzyldimethylhexadecylammonium chloride (BHDACl), hexadecylpyridinium bromide (HPyBr), hexadecylpyridinium chloride (HPyCl), and their mixtures with anionic polyelectrolytes, namely carboxymethylcellulose sodium salt (CMC) and polystyrene sulfonate sodium salt (PSS) were studied with the help of conductivity (κ), viscosity (η), turbidity (τ), and NMR studies. κ showed single aggregation process, which was represented by apparent critical micelle concentration, *acmc*, of each surfactant in aqueous polyelectrolyte solution. Both η and τ demonstrated strong electrostriction effects in the case of BHDACl-polyelectrolyte systems due to weak electrostatic interactions in view of steric hindrances created by benzylic group of BHDACl. ^{1}H NMR results showed that the head group proton resonances of BHDACl upon incorporation of HPyBr or HPyCl in the presence of CMC or PSS remained identical to that in pure water, which demonstrated very weak interactions between BHDACl and polyelectrolytes. A less shielding of pyridinium head group protons by BHDACl in the presence of polyelectrolytes in comparison to that in pure water indicated favorable electrostatic interactions between pyridinium head groups and anionic polyelectrolytes. HPyBr in comparison to HPyCl showed stronger interactions with polyelectrolytes.

Keywords Cationic surfactants · Mixed micelles · Anionic polyelectrolytes · Micelles-polyelectrolyte interactions

Introduction

Mixtures of surfactants, often in conjunction with polymers, are used widely in industrial and domestic formulations. A surfactant may help in surface tension lowering, wetting, active ingredient deposition, and control of stability or rheology, but its properties generally change in the complex mixture. Understanding of the interactions between the components of a surfactant mixture is, therefore, crucial to optimizing their performance. Thus, a significant research has been focused on the field of polymer-surfactant interactions in recent decades and several reviews exist [1, 2, 3, 4]. The case of polymer-surfactant pairs in which the polymer is a polyion and the surfactant is also ionic but bears the opposite charge is of special interest. If the respective charges are of the same sign, association between the polymer and the surfactant is expected to be weak or absent. A combination of cationic surfactant and anionic polyelectrolyte is an example of strongly interacting system with extraordinary solution properties [5, 6, 7]. Fundamentally, the driving force of electrostatic interactions depends upon several factors. Of these, the nature of cationic surfactant head group is the main contributing factor which screens the electrostatic interactions significantly if it is bulky in nature [8, 9]. For instance, if we compare the electrostatic interactions of tetraalkylammonium head group and pyridinium head group cationic surfactants with same polymer, the latter would have stronger interactions in comparison to the former [9]. The pioneering work of Saito [10, 11, 12] established that surfactant-polymer ratio is another criteria which governs the overall interactions. At a low ratio when surfactant is essentially in the monomeric form, the binding is due to the dipolar interactions of surfactant head group with polar sites on the polymer backbone. At a high ratio, when apart from monomers, micelles are also present, the structure of micelle-polymer complex becomes quite difficult to establish.

At this end, the present account deals with strongly interacting cationic surfactants, namely BHDACl, HPyBr, HPyCl, and their mixtures with anionic polyelectrolytes such as CMC and PSS. Though, the surfactants belong to a category of cationic surfactants with identical hydrophobic tails, the presence of benzylic and pyridinium head groups is expected to induce significant differences in the surfactant-polymer interactions. The physiochemical properties of these systems have been explored with the help of conductivity (κ), viscosity (η), turbidity (τ), and NMR studies. κ is quite useful to evaluate the micellar properties [13, 14, 15] of ionic surfactants. η [16, 17] gives major insight in the mode of surfactant-polymer association particularly when this association is mainly influenced by electrostriction effects. τ helps [18, 19, 20] in exploring the concentration range of both surfactant and polymer where insoluble salt formation takes place. One can always pinpoint the origin of driving forces responsible for such kind association from NMR studies. NMR methods have demonstrated considerable, and sometimes fundamental contributions to the physiochemical properties of surfactants [21, 22].

Experimental

BHDACl, 98% pure from TCI, Japan, HPyBr and HPyCl, all more than 99% pure from Lancaster Synthesis, England, were used as received. CMC, average molecular weight 100,000, and PSS, average molecular weight 70,000, were obtained from TCI, Japan. Triply distilled conductivity water was used in the preparation of all solutions. All solutions were prepared by mass within the accuracy of ±0.01 mg. The mole fractions were accurate to ±0.0001 units.

The conductivity measurements were carried out with the help of digital conductivity meter. The efflux times of dilute solutions of single and mixed surfactant systems were determined with the help of Ubbelohde type suspended level capillary viscometer. From the ratio of efflux times of the test solution (t) to that of the reference solution (t_o), the relative viscosity can be calculated ($\eta_r = t/t_o$) by ignoring the density corrections for the dilute solutions and subsequently specific viscosity ($\eta_{sp} = \eta_r - 1$). The turbidity (τ) measurements for all the present systems were performed by using Nephelo-Turbidity meter, Type 131, Systronics, India. This instrument worked on the basis of scattering of light by the colloidal particles.

The details of κ, η_r, and τ, measurements have been reported elsewhere [18]. All measurements were carried out at 25±0.05 °C.

NMR measurements ^{1}H NMR spectra were run on Bruker AC200E instrument. All chemical shifts were measured relative to sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS), which acted as an internal standard. At certain mole fractions, deep turbid solutions were first filtered and the NMR of clear solutions were taken. Deuterium oxide (D_2O), 99.9%D from Aldrich was used as solvent instead of water to weaken the water signal for all solutions and the chemical shifts were measured as a function of added type. Note that the surfactant concentrations were always higher than the *acmc* and 0.005% w/v of each polyelectrolyte was used for NMR studies. The chemical shift differences were only considered in this study. A downfield shift is represented by a negative sign ($-\Delta\delta$) and an upfield shift is shown by a positive sign ($+\Delta\delta$).

Results and discussion

Conductivity behavior

Figure 1i shows some representative κ plots. The critical micelle concentration (*cmc*) and apparent critical micelle concentration (*acmc*) values from these plots were calculated as explained before [23]. A graphical representation of *acmc* in aqueous polymer solutions has been shown in Fig. 1ii,iii. In all cases, *acmc* values over the whole mole fraction range show a non-linear variation. Clint equation in the following form can be used to identify the ideality in the mixed micelle formation [24]

$$\frac{1}{cmc^*} = \frac{\alpha_1}{cmc_1} + \frac{(1-\alpha_1)}{cmc_2} \tag{1}$$

where α_1 is the mole fraction of surfactant 1 (BHDACl) in total mixed solute, cmc_1 and cmc_2 are the critical micelle concentrations of components 1 and 2, in pure water respectively. The cmc^* values represent the ideal state values thus calculated have also been plotted in Fig. 1ii,iii. Similar equation can be used for the binary mixtures in aqueous polyelectrolyte solutions by replacing *cmc* with *acmc* values. One would see that *cmc* and *acmc* values in all cases always lower than the corresponding cmc^* and $acmc^*$ values. The free energy of micelle formation $\left(\Delta G_m^o = RT\ln X_{cmc} \text{ or } RT\ln X_{acmc}\right)$ was evaluated for each pure surfactant and their 1:1 mixtures in pure water as well as in aqueous polyelectrolyte solutions (Table 1). It is to be mentioned here that counterion binding is not considered in evaluating ΔG_m^o since in oppositely charged cationic surfactants and anionic polyelectrolytes as in the case of present systems, counterion binding is expected to contribute very little. In each case, ΔG_m^o was slightly less negative in the presence of CMC and PSS with greater magnitude of transfer of free energy from pure water to aqueous

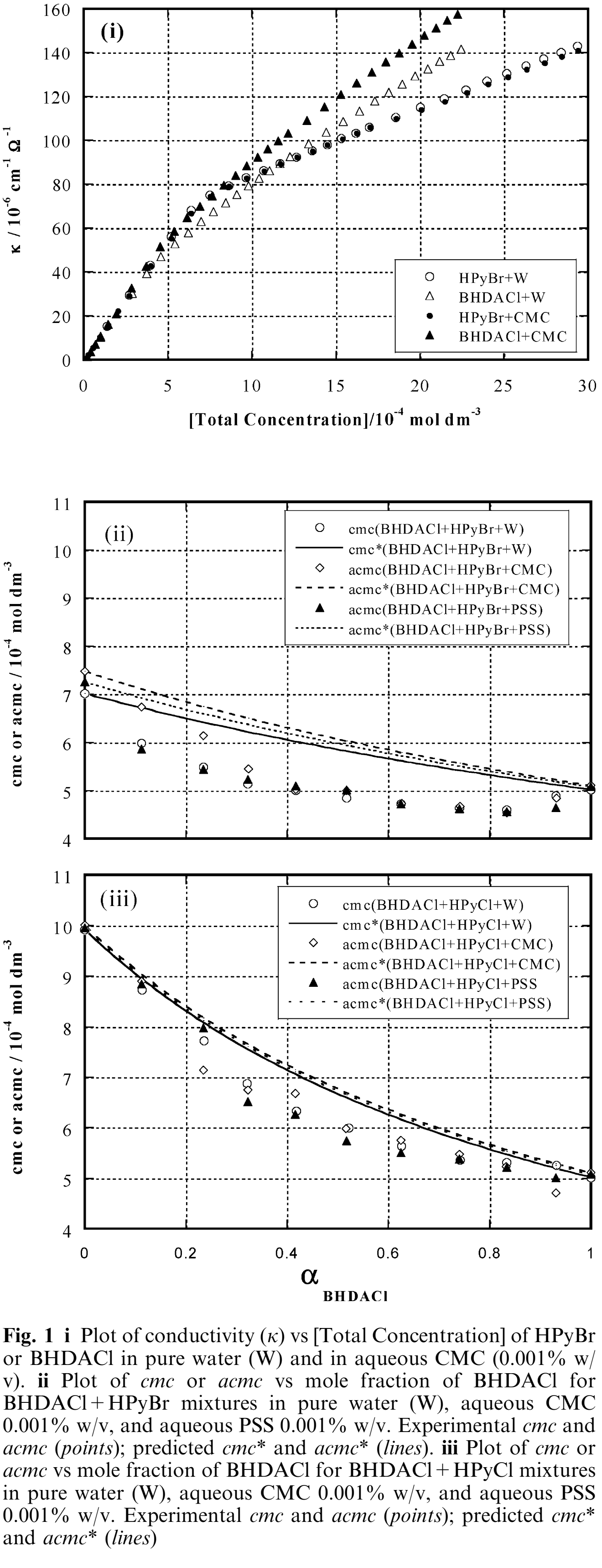

Fig. 1 **i** Plot of conductivity (κ) vs [Total Concentration] of HPyBr or BHDACl in pure water (W) and in aqueous CMC (0.001% w/v). **ii** Plot of *cmc* or *acmc* vs mole fraction of BHDACl for BHDACl + HPyBr mixtures in pure water (W), aqueous CMC 0.001% w/v, and aqueous PSS 0.001% w/v. Experimental *cmc* and *acmc* (*points*); predicted *cmc** and *acmc** (*lines*). **iii** Plot of *cmc* or *acmc* vs mole fraction of BHDACl for BHDACl + HPyCl mixtures in pure water (W), aqueous CMC 0.001% w/v, and aqueous PSS 0.001% w/v. Experimental *cmc* and *acmc* (*points*); predicted *cmc** and *acmc** (*lines*)

polyelectrolyte for HPyBr than BHDACl or HPyCl (not shown). Macdonald et al. [25] have also observed similar mixed micellar behavior of cationic + zwitterionic surfactants in the presence of PSS. It is also possible to evaluate degree of binding (β) of cationic micelles to polyelectrolyte, which is given by the ratio of amount of surfactant bound to the monomolar concentration of a polyelectrolyte. A difference between the *acmc* 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 which has been complexed to polyelectrolyte would correspond to the difference between the *acmc* and *cmc*. β values thus evaluated for pure surfactants and their 1:1 mixtures have been listed in Table 1. One would see that these values are much higher for HPyBr and that too in aqueous CMC rather than aqueous PSS. Therefore, the κ results demonstrate that HPyBr has stronger electrostatic interactions in comparison to BHDACl or HPyCl with polyelectrolytes.

Viscometric and turbidity behaviors

Figure 2i shows a variation of η_{sp} with respect to α_{BHDACl} for BHDACl + HPyBr/HPyCl mixtures in pure water as well as in the presence of CMC and PSS. It demonstrates that the presence of CMC and PSS leads to an almost additively rule for both binary mixtures unlike to that in pure water. It suggests that a variation in the morphology of mixed micelles with respect to a change in composition is predominantly overshadowed by strong cationic micelle-anionic polyelectrolyte interactions. This is also evident from the τ measurements (Fig. 2ii), which are sensitive to the insoluble salt formation. τ values for both mixtures are close to zero in pure water but rise in the presence of polyelectrolyte. However, there is no constant increase in τ over the whole mole fraction range but the values are much higher in the HPyBr or HPyCl rich regions and highest in the former case. It indicates that the following order of interaction of surfactants with CMC and PSS exists HPyBr > HPyCl > BHDACl.

η_{sp} and τ investigations leading to the micelle formation by BHDACl, HPyBr, and HPyCl have been demonstrated in Fig. 3. The strong electrostriction effects are believed to be responsible for higher [26, 27, 28] η_{sp} and lower τ for BHDACl in aqueous polymer (Fig. 3i and Fig. 3iv, respectively) in comparison to those for HPyBr or HPyCl. The electrostriction effects are generally produced by the electroactive sites of solute molecules available for electrostatic interactions with water dipoles. This may be possible only when opposite polarities of cationic micelles and anionic polyelectrolytes are not completely neutralized. This will produce higher η_{sp} due to strong electrostriction effects and lower

Table 1 Values of *cmc* or *acmc*/10^{-4} mol dm^{-3} from κ and η_{sp} measurements; standard free energy of micelle formation (ΔG_m^o) and degree of binding (β) evaluated from κ data for BHDACl, HPyBr, HPyCl, and their 1:1 mixtures in the presence of CMC and PSS

	Water			CMC				PSS			
	cmc			*acmc*				*acmc*			
	κ	η_{sp}	(ΔG_m^o)	κ	η_{sp}	(ΔG_m^o)	β_{CMC}	κ	η_{sp}	(ΔG_m^o)	β_{PSS}
BHDACl	5.02 ±0.24	5.8	−28.8	5.11 ±0.13	-	−28.7	0.32	5.08 ±0.21	5.37	−28.7	0.12
HPyCl	9.92 ±0.26	11.8	−27.1	10.00 ±0.30	9.18	−27.1	0.28	9.95 ±0.26	9.46	−27.1	0.06
HPyBr	7.02 ±0.01	9.6	−27.9	7.48 ±0.12	6.55	−27.8	1.60	7.26 ±0.14	6.47	−27.9	0.50
BHDACl + HPyBr (1:1)	4.84 ±0.15	-	−28.9	5.00 ±0.15	-	−28.8	0.57	5.01 ±0.19	-	−28.8	0.35
BHDACl + HPyCl (1:1)	5.99 ±0.19	-	-28.3	5.98 ±0.24	-	−28.3	-	5.94 ±0.25	-	−27.4	-

β values computed from the *cmc* and *acmc* values evaluated from κ measurements

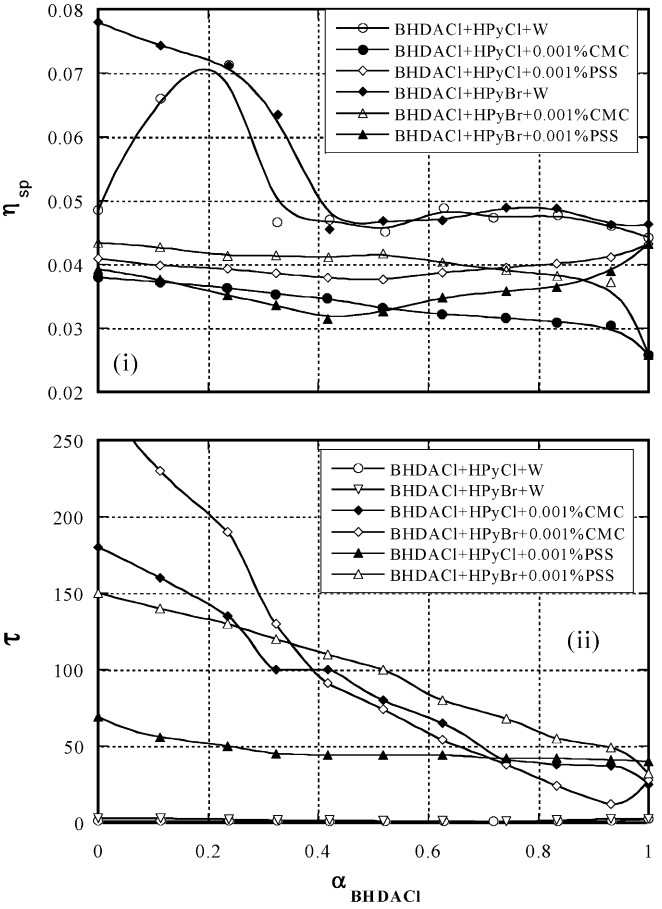

Fig. 2 i Plot of η_{sp} vs mole fraction of BHDACl for BHDACl + HPyBr and BHDACl + HPyCl mixtures in pure water (W), aqueous CMC 0.001% w/v, and aqueous PSS 0.001% w/v. **ii** Plot of τ vs mole fraction of BHDACl for BHDACl + HPyBr and BHDACl + HPyCl mixtures in pure water (W), aqueous CMC 0.001% w/v, and aqueous PSS 0.001% w/v

τ values as in the case of BHDACl + polyelectrolyte systems. On the contrary, a large decrease in the η_{sp} (Fig. 3ii,iii) and increase in the τ (Fig. 3v,vi) for HPyBr and HPyCl in the presence of polyelectrolytes may be attributed to a large decrease in the electrostriction effects upon micelle-polyelectrolyte favorable complexation which lead to the insoluble salt formation. A decrease in the η_{sp} may be attributed to the coiling of polyelectrolyte backbone around surfactant aggregates as reported in the case of dodecyltrimethylammonium bromide + PSS [3, 29]. Each η_{sp} plot in the presence of CMC and PSS shows a sharp minimum (Fig. 3ii,iii, inset) representing an *acmc* value. The *acmc* values thus evaluated have been compared with those obtained from κ measurements in Table 1. Both sets of values are found to be in good agreement with each other. Similar results have already been reported in the literature [3]. Figure 4 demonstrates a variation in the reduced viscosity (η_{red}) and turbidity (τ_{red}) of all present systems upon increasing the amount of CMC and PSS. Figure 4i shows that η_{red} is much higher in the case of BHDACl + CMC system in comparison to all other, whereas no distinction can be made in the case of surfactant + PSS systems(Fig. 4ii). τ_{red} is highest in the cases of HPyBr + CMC (Fig. 4iii) and HPyBr + PSS (Fig. 4iv). Both η_{red} and τ_{red} results indicate that BHDACl has least interactions with CMC whereas HPyBr has strongest interactions with CMC as well as PSS.

NMR behavior

^{1}H signals of pure and mixed components of BHDACl + HPyBr/HPyCl mixtures over whole mole fraction range were studied while keeping the total surfactant concentration constant 3 mmol/l in each

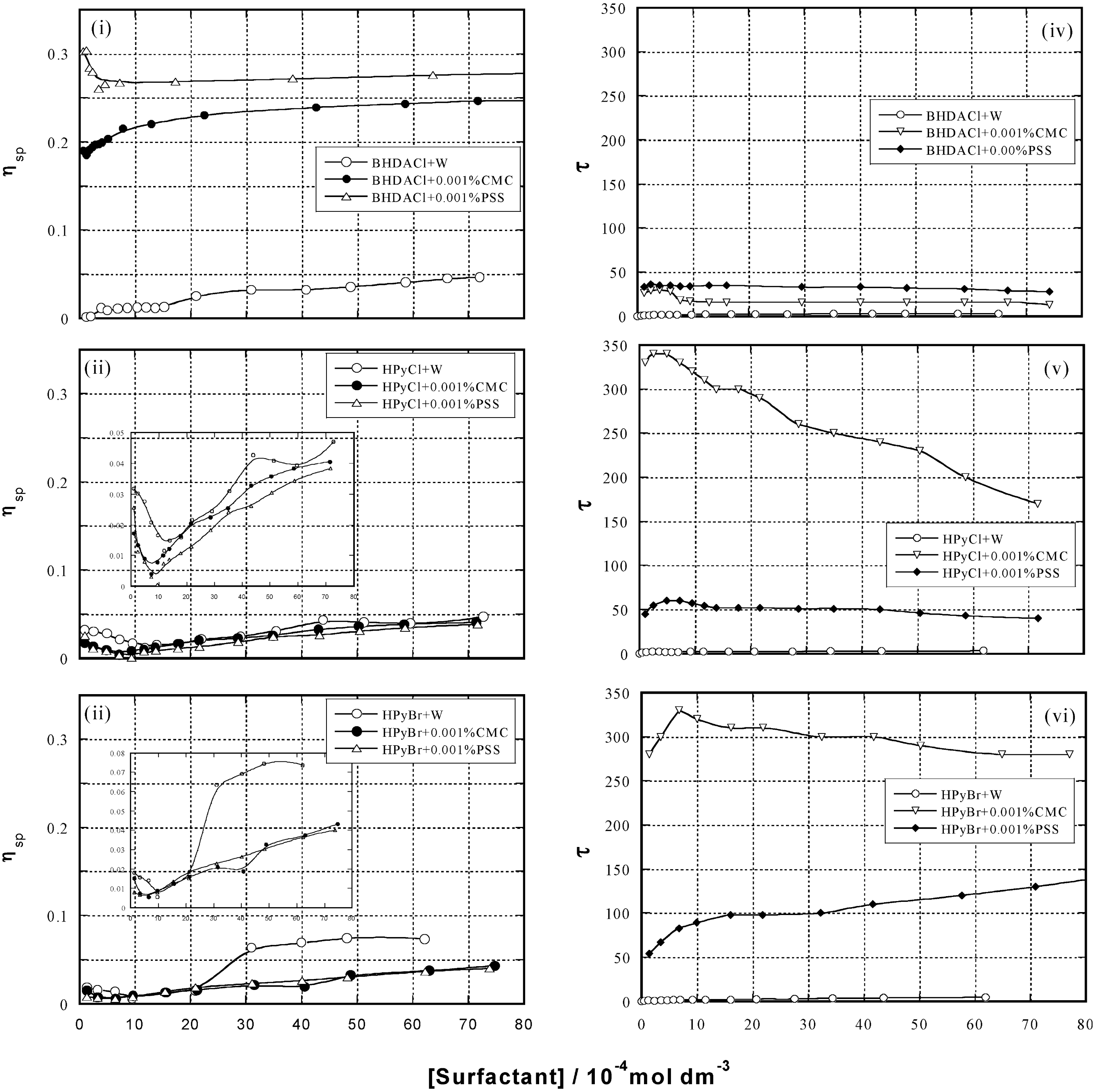

Fig. 3 i Plot of η_{sp} vs [Total concentration] of BHDACl in pure water (W), aqueous CMC 0.001% w/v, and aqueous PSS 0.001% w/v. **ii** Plot of η_{sp} vs [Total concentration] of HPyCl in pure water (W), aqueous CMC 0.001% w/v, and aqueous PSS 0.001% w/v. **iii** Plot of η_{sp} vs [Total concentration] of HPyBr in pure water (W), aqueous CMC 0.001% w/v, and aqueous PSS 0.001% w/v. **iv** Plot of τ vs [Total concentration] of BHDACl in pure water (W), aqueous CMC 0.001% w/v, and aqueous PSS 0.001% w/v. **v** Plot of τ vs [Total concentration] of HPyCl in pure water (W), aqueous CMC 0.001% w/v, and aqueous PSS 0.001% w/v. **vi** Plot of τ vs [Total concentration] of HPyBr in pure water (W), aqueous CMC 0.001% w/v, and aqueous PSS 0.001% w/v

binary mixture. The formulas and proton numbering of BHDACl, HPyBr, and HPyCl are shown in Fig. 5.

The variations of ^{1}H NMR chemical shifts are listed in Tables 2, 3, 4, and 5. A careful analysis of various ^{1}H signals in the case of pure components and a shift in the position of these signals upon mixing will help us to deduce the relative arrangement of unlike surfactant monomers in the mixed state along with the polyelectrolyte macromolecules. Although the observed chemical shift is the weighted average of those of the monomer and the micellar molecules, these changes in chemical shift are

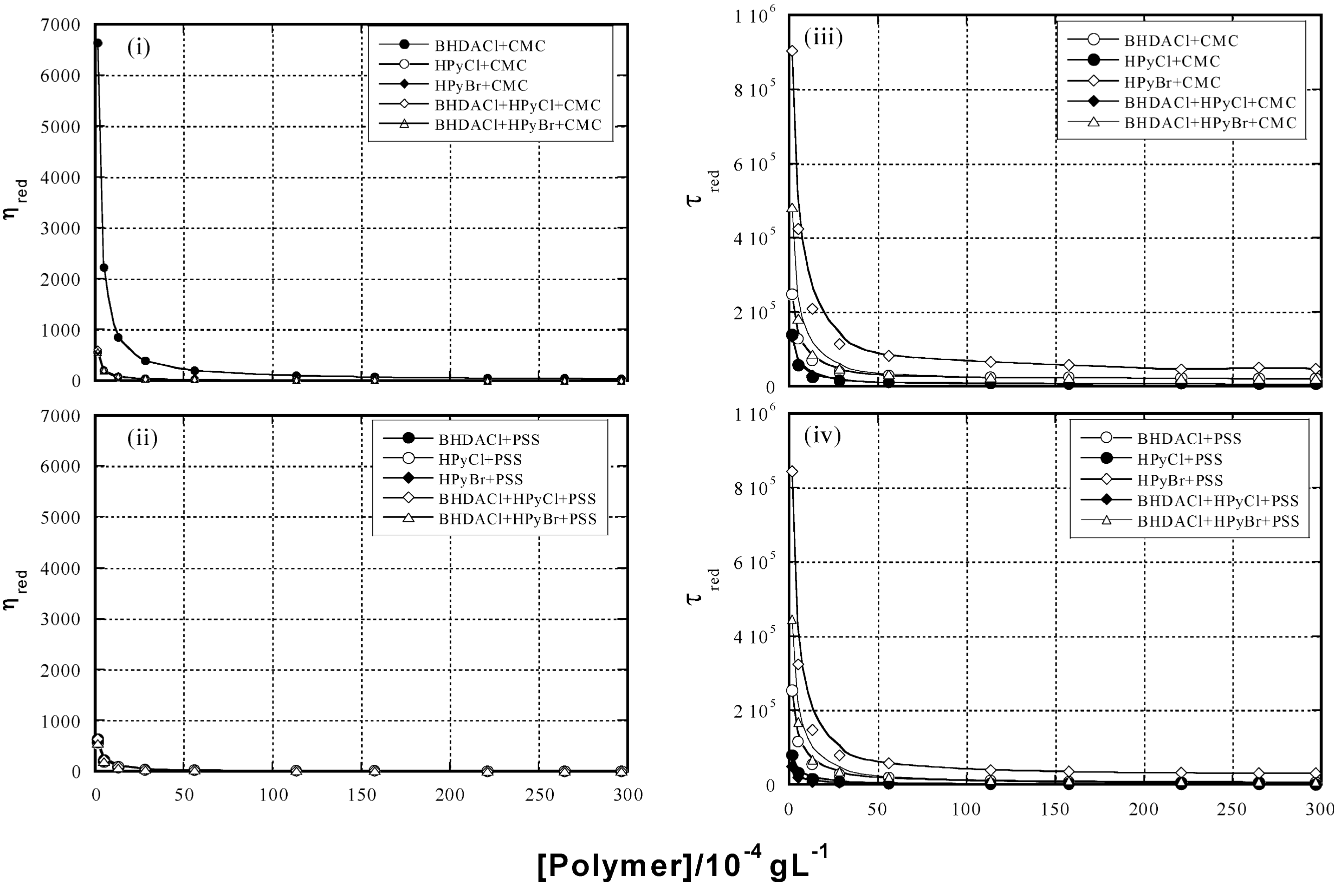

Fig. 4 i Plot of η_{red} vs [Polymer] of BHDACl, HPyBr, HPyCl, BHDACl + HPyBr, and BHDACl + HPyCl mixtures in aqueous CMC. **ii** Plot of η_{red} vs [Polymer] of BHDACl, HPyBr, HPyCl, BHDACl + HPyBr, and BHDACl + HPyCl mixtures in aqueous PSS. **iii** Plot of τ_{red} vs [Polymer] of BHDACl, HPyBr, HPyCl, BHDACl + HPyBr, and BHDACl + HPyCl mixtures in aqueous CMC. **iv** Plot of τ_{red} vs [Polymer] of BHDACl, HPyBr, HPyCl, BHDACl + HPyBr, and BHDACl + HPyCl mixtures in aqueous PSS

different for different protons in the same molecule. In particular, it is also expected that the benzylic group of BHDACl will induce significant shift in the proton resonance of cosurfactants (CS, i.e., HPyBr or HPyCl) due to the anisotropy of its magnetic properties on the basis of ring current effects [30, 31, 32, 33, 34].

Figure 6i–iii represents a variation in the chemical shifts of head group protons of BHDACl i.e., *Ba*, *Bb*, and *Bc* with respect to an increase in the amount of CS. Almost all BHDACl head group protons undergo a downfield shift with an increase in the fraction of CS, which suggests that the mutual ring currents of benzylic groups fade away upon intercalation of pyridinium head groups of CS in the course of mixed micellization. Interestingly, there is not much difference between the $\Delta\delta$ value in the absence as well as presence of CMC or PSS. A qualitative comparison among *Ba*, *Bb*, and *Bc* suggests that *Bb* protons undergo maximum downfield shift up to $\alpha_{cs} = 0.8$, which seems to be obvious in view of its proximity to the center of adjoining aromatic ring of benzylic group. On the other hand, head group protons of HPyBr and HPyCl, i.e., *Zd, Ze, Zf, Xd, Xe,* and *Xf* (Fig. 6iv–vi) have undergone an upfield shift with the increase in the amount of BHDACl and this behavior is complementary to that of head group protons of BHDACl, i.e., *Ba, Bb,* and *Bc* (Fig. 6i–iii). It suggests that the mutual deshielding of *Ba*, *Bb*, and *Bc* in fact brings about the shielding on *Zd, Ze, Zf, Xd, Xe*, and X*f* owing to ring currents of benzylic groups. Mandal et. al. [35] reported that the solublization of 2,6-di-*tert*-butyl-4-methylphenol and 2- or 3-*tert*-butyl-4-methoxyphenol in the head group region of hexadecyltrimethylammonium bromide (HTAB) and chloride induced shielding effects due to ring currents. Bhatt and Gaikar [36] also observed the intercalation of butyl benzene sulfonate in between the HTAB head groups and which shields the later due to ring current effects. Furthermore, a close inspection of Fig. 6iv–vi demonstrates that there is significant difference in the shielding effects of head group protons of CS upon incorporation of BHDACl in the absence as well as in the presence of CMC and PSS. *Zd* protons of HPyBr experience relatively much less shielding in the presence of CMC and PSS especially in the HPyBr rich region of the mixture in comparison to

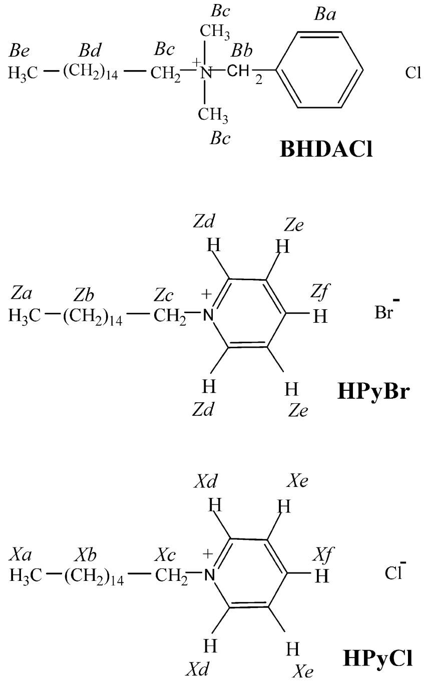

Fig. 5 Formulas and proton labeling of BHDACl, HPyBr, and HPyCl molecules

Table 2 ^{1}H chemical shifts (ppm) of mixed BHDACl(*B*) and HPyCl(*X*) in aqueous 0.005% w/v CMC

	α_{BHDACl}					
	0.0	0.2	0.4	0.6	0.8	1.0
Xa	0.838	0.867	0.886	0.893	0.909	
Xb	1.238	1.264	1.278	1.290	1.308	
Xc	2.073	2.018	1.843	1.835	1.790	
Xd	9.038	8.975	8.948	8.936	8.865	
Xe	8.214	8.154	8.126	8.105	8.073	
Xf	8.768	8.732	8.727	8.711	8.680	
Ba		7.522	7.499	7.491	7.483	7.450
Bb		4.681	4.627	4.595	4.534	4.480
Bc		3.182	3.149	3.128	3.091	3.042
Bd		1.264	1.278	1.290	1.308	1.335
Be		0.867	0.886	0.893	0.909	0.936

Table 3 ^{1}H chemical shifts (ppm) of mixed BHDACl(*B*) and HPyBr(*Z*) in aqueous 0.005% w/v CMC

	α_{BHDACl}					
	0.0	0.2	0.4	0.6	0.8	1.0
Za	0.834	0.879	0.896	0.908	0.916	
Zb	1.237	1.279	1.291	1.306	1.317	
Zc	2.104	2.042	1.837	1.832	1.827	
Zd	9.096	9.019	8.986	8.879	8.869	
Ze	8.213	8.154	8.125	8.119	8.108	
Zf	8.688	8.610	8.591	8.573	8.546	
Ba		7.545	7.511	7.484	7.481	7.450
Bb		4.687	4.637	4.598	4.557	4.480
Bc		3.197	3.156	3.112	3.097	3.042
Bd		1.279	1.291	1.306	1.317	1.335
Be		0.879	0.896	0.908	0.916	0.936

Table 4 ^{1}H chemical shifts (ppm) of mixed BHDACl(*B*) and HPyCl(*X*) in aqueous 0.005% w/v PSS

	α_{BHDACl}					
	0.0	0.2	0.4	0.6	0.8	1.0
Xa	0.872	0.891	0.893	0.908	0.918	
Xb	1.265	1.277	1.289	1.304	1.316	
Xc	2.057	1.950	1.853	1.842	1.788	
Xd	9.018	8.949	8.898	8.828	8.799	
Xe	8.208	8.140	8.127	8.108	8.078	
Xf	8.650	8.608	8.584	8.488	8.434	
Ba		7.523	7.510	7.481	7.463	7.441
Bb		4.596	4.586	4.556	4.518	4.463
Bc		3.163	3.135	3.107	3.081	3.037
Bd		1.277	1.289	1.304	1.316	1.337
Be		0.891	0.893	0.908	0.918	0.936

Table 5 ^{1}H chemical shifts (ppm) of mixed BHDACl(*B*) and HPyBr(*Z*) in aqueous 0.005% w/v PSS

	α_{BHDACl}					
	0.0	0.2	0.4	0.6	0.8	1.0
Za	0.833	0.864	0.880	0.902	0.917	
Zb	1.239	1.265	1.281	1.301	1.316	
Zc	2.074	1.995	1.977	1.830	1.808	
Zd	9.062	9.033	8.998	8.976	8.913	
Ze	8.200	8.128	8.121	8.096	8.001	
Zf	8.670	8.649	8.645	8.576	8.557	
Ba		7.520	7.499	7.481	7.467	7.441
Bb		4.597	4.588	4.576	4.547	4.463
Bc		3.202	3.164	3.124	3.093	3.037
Bd		1.265	1.281	1.301	1.316	1.337
Be		0.864	0.880	0.902	0.917	0.936

that in pure water (Fig. 6iv). In the BHDACl rich region, Zd and Xd proton resonance in the presence of CMC even exceed the value in pure water. It clearly indicates that CMC undergoes stronger interactions than PSS. However, this effect is not so significant in the case of *Ze* and *Xe* (Fig. 6v). Similar variation is also shown by *Zf* and *Xf* in the CS rich region of the mixture (Fig. 6vi).

The hydrocarbon tail protons of BHDACl, i.e., *Bd* and *Be* (Fig. 7i,ii) in the presence of CS in pure water first undergo a weak downfield shift up to $\alpha_{cs} = 0.2$ and then upfield shift afterwards. The downfield shift can be attributed to the intercalation of bulky pyridinium head group in the head group region of mixed micelle with the result of which it leads to the formation of loose mixed micelles. This will bring the alkyl chain away from the ring current effect of benzylic groups

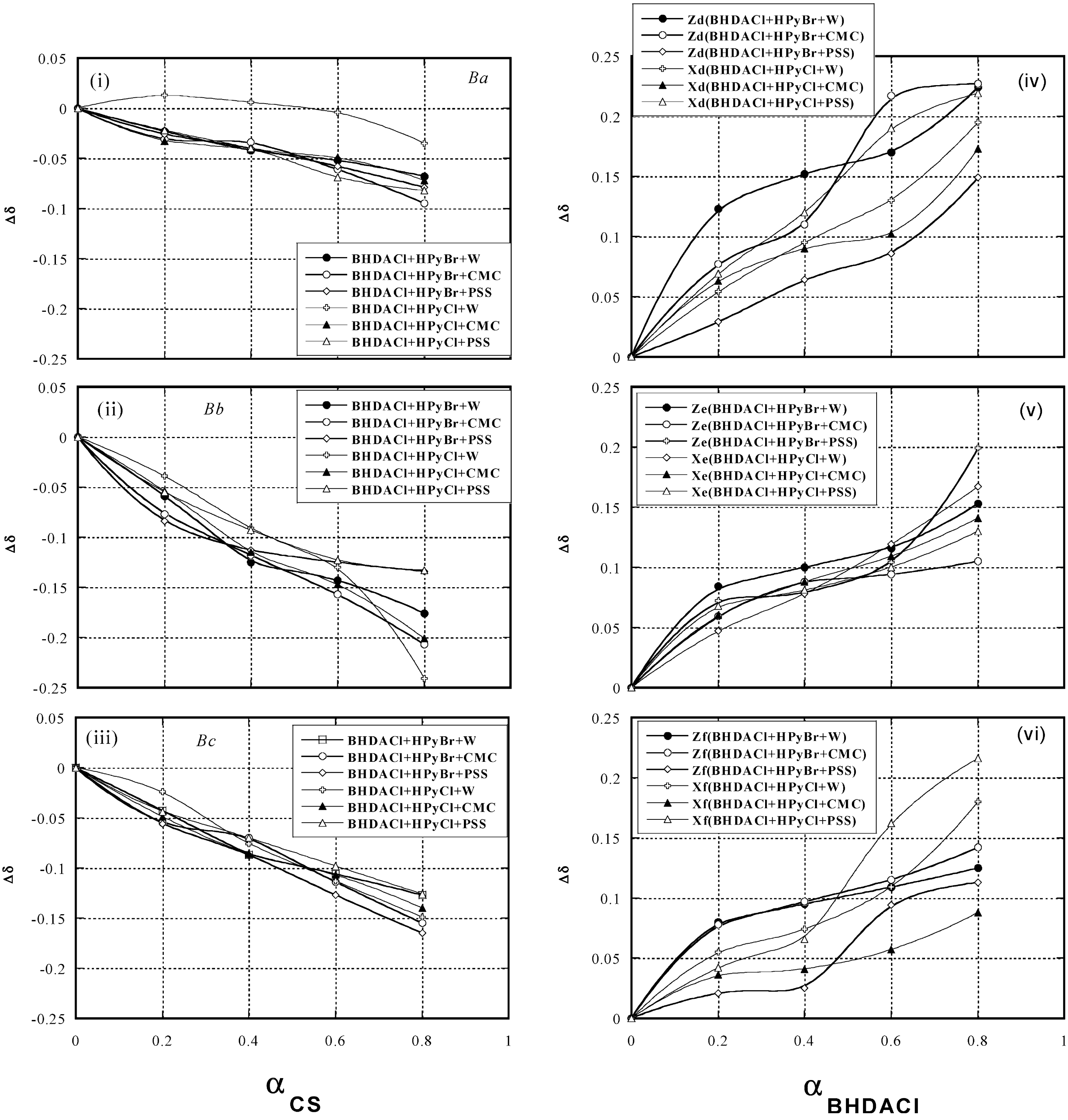

Fig. 6 i–iii ^{1}H chemical shifts (ppm) of BHDACl head group protons, i.e., *Ba, Bb, Bc*, respectively, vs mole fraction of cosurfactants (α_{cs}) for BHDACl+ HPyBr/HPyCl mixtures in pure water as well as in the presence of 0.005% w/v CMC and PSS; **iv–vi** ^{1}H chemical shifts (ppm) of HPyBr and HPyCl head group protons, i.e., *Zd, Xd; Ze, Xe*; and *Zf, Xf*, respectively, vs mole fraction of BHDACl (α_{BHDACl}) for BHDACl+HPyBr/HPyCl mixtures in pure water as well as in the presence of 0.005% w/v CMC and PSS

due to internal packing constraints [37, 38]. Furthermore, the additive effect of HPyCl produces stronger deshielding in comparison to HPyBr due to weakly associated Cl^- in comparison to strongly bound Br^- counterions. However, further increase in the amount of CS will result in the predominance of hydrophobic interactions with the result of which no further downfield shift is observed and leads to a continuous shielding of *Bd* and *Be* protons. Interestingly, in the

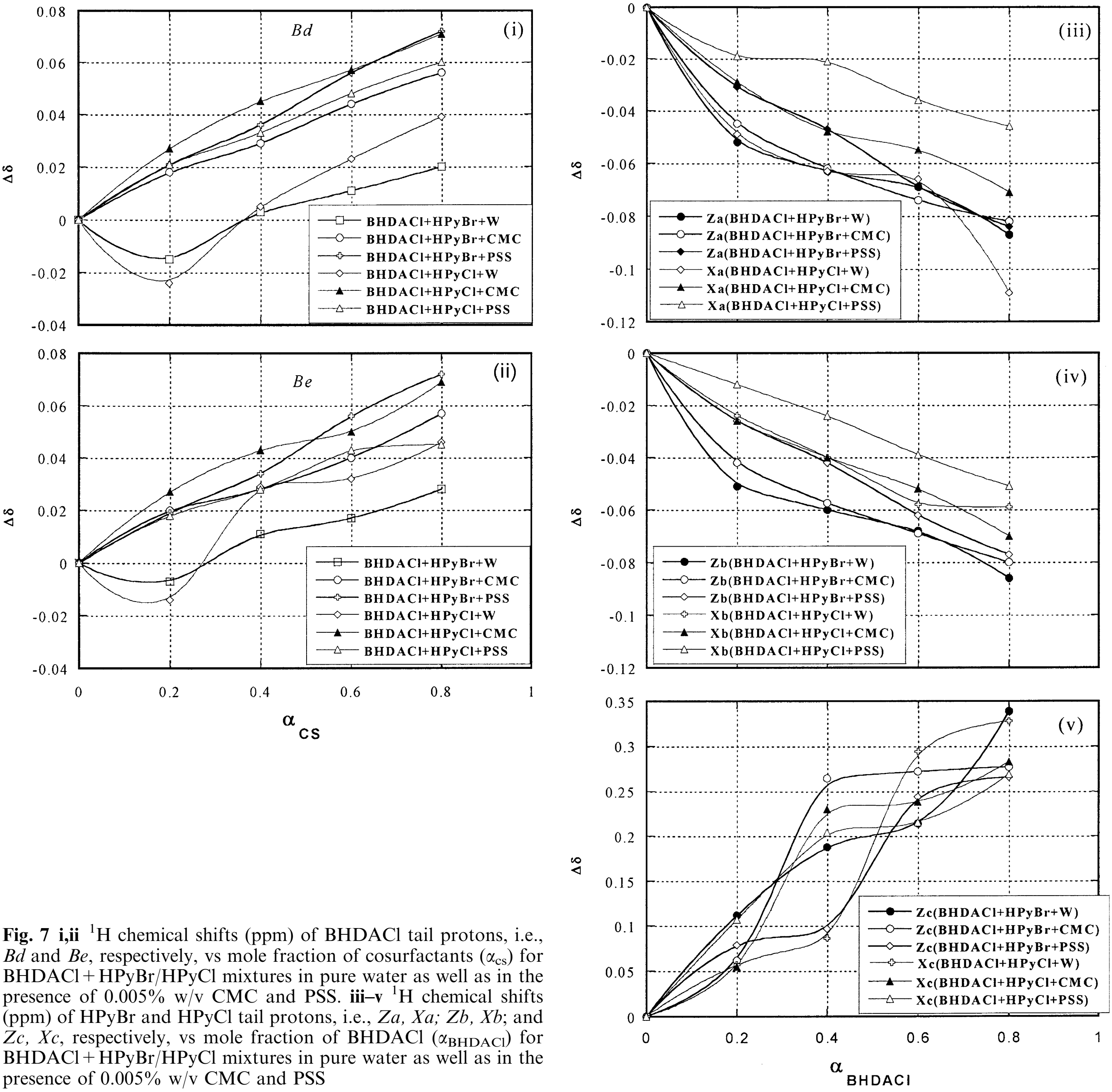

Fig. 7 i,ii ^{1}H chemical shifts (ppm) of BHDACl tail protons, i.e., *Bd* and *Be*, respectively, vs mole fraction of cosurfactants (α_{cs}) for BHDACl + HPyBr/HPyCl mixtures in pure water as well as in the presence of 0.005% w/v CMC and PSS. **iii–v** ^{1}H chemical shifts (ppm) of HPyBr and HPyCl tail protons, i.e., *Za, Xa; Zb, Xb*; and *Zc, Xc*, respectively, vs mole fraction of BHDACl (α_{BHDACl}) for BHDACl + HPyBr/HPyCl mixtures in pure water as well as in the presence of 0.005% w/v CMC and PSS

presence of CMC and PSS no downfield shift is observed in the case of *Bd* and *Be* proton resonance and instead of it, a continuous shielding of these protons occurs. A closeness of the curves does not allow us to differentiate between the additive effect of CMC and PSS. A continuous increase in the Δ*δ* value of *Bd* and *Be* can be attributed to the preferential electrostatic interactions of CS with CMC and PSS which would decrease steric effects and thus produce compact mixed micelles. On the other hand, almost equal magnitude of deshielding of *Za, Zb, Xa*, and *Xb* protons can be observed upon induction of BHDACl in the micelles of CS (Fig. 7iii,iv), which is obviously due to the formation of loose mixed micelle and is also evident from Fig. 7v.

Above results demonstrate that the additive effect of anionic polyelectrolytes is very weak on the proton resonance of BHDACl (Fig. 6i–6iii). It means that BHDACl has relatively weak interactions with polyelectrolytes. *η* and *τ* plots in Figs. 3 and 4 also share similar information. It may be attributed to the fact that benzylic group present in the head group region of BHDACl induces steric hindrances for an anionic polyelectrolyte in the course of electrostatic interactions driven by opposite polarities. On the contrary, a decrease in the shielding effects of *Zd* protons in the presence of CMC or PSS (Fig. 6iv) could be due to the displacement of benzylic group away from the polymer backbone in the course of stronger electrostatic interactions between the pyridinium head group and polyelectrolytes.

Conclusions

The present study demonstrates that HPyBr followed by HPyCl have stronger interactions in comparison to BHDACl, with anionic polyelectrolytes such as CMC and PSS. It has been concluded that the presence of benzylic group in the head group region of BHDACl creates steric hindrances in the course of electrostatic interactions between BHDACl and anionic polyelectrolytes which is fully supported by NMR studies. A weak association is also evident from the strong electrostriction effects as well as low turbidity values than those for HPyBr and HPyCl.

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