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Unlike surfactant–polymer interactions of sodium dodecyl sulfate and sodium dodecylbenzene sulfonate with water-soluble polymers

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Abstract Single and mixed micelle formation by sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (SDBS) and their mixtures in pure water and in the presence of water-soluble polymers such as Synperonic 85 (triblock polymer, TBP), hydroxypropylcellulose (HPC), and carboxymethylcellulose sodium salt (CMC) were studied with the help of conductivity, pyrene fluorescence, cyclic voltammetry, and viscosity measurements. Conductivity measurements showed a single aggregation process for pure surfactants and their mixtures both in pure water as well as in the presence of water-soluble polymers. Triple breaks corresponding to two aggregation processes for SDS, SDBS, and their mixture in the presence of TBP were observed from fluorescence measurements. The first one demonstrated the critical aggregation process due to the adsorption of surfactant monomers on TBP

macromolecule. The second one was attributed to the participation of surfactant–polymer aggregates formed at the first one, in the micelle formation process. The aggregation number (N_{agg}) of single and mixed micelles and diffusion coefficient (D) of electroactive probe were computed from the fluorescence and cyclic voltammetry measurements, respectively. Both parameters, along with the viscosity results, indicated stronger SDS–polymer interactions in comparison to SDBS–polymer interactions. Mixed surfactant–polymer interactions showed compensating effects of both pure surfactants. The nature of mixed micelles was found to be ideal in all cases, as evaluated by applying the regular solution and Motomura's approximations.

Keywords Anionic surfactants · Mixed micelles · Water-soluble polymers · Mixed micelle–polymer interactions

Introduction

In the field of colloidal chemistry, surfactant–polymer interactions [1] have become increasingly important in view of their large industrial applications. Although a lot of work has been devoted to this field, still the complex nature of such interactions has not been fully understood. In the case of charged polymers, it is

comparatively easy to understand the electrostatic interactions between ionic surfactants and oppositely charged polymers, as in the case of anionic surfactants–cationic starch [2] and alkyltrimethylammonium bromides–sodium poly(styrene sulfonate) systems [3]. But the situation becomes quite intriguing and complex in the case of neutral polymers such as poly(ethylene oxide) (PEO), poly(ethylene glycol), poly(vinyl pyrroli-

done), and hydroxy propylcellulose [4]. In the case of both categories, the surfactant–polymer interactions depend upon several factors such as the nature of surfactant head group, polar groups embedded in the polymer backbone, polymer hydrophobicity, and flexibility etc. [4, 5]. It has also been observed that anionic surfactants, in comparison to cationic ones, have stronger interactions with neutral polymers [4, 6]. The stronger interactions have been ascribed on the basis of both electrostatic as well as non-electrostatic interactions prevailing between the surfactant and polymer. The origin of electrostatic interactions between an anionic surfactant and a neutral water-soluble polymer like PEO can be attributed to the presence of electronegative potential on the PEO chain, which undergoes electrostatic interactions with electropositive counterions (for example Na^+ ions) of SDS or SDBS to form a "pseudopolycation" in which positive charges are distributed along the polymer coil. This charge distribution along the polymer chain helps in the anionic surfactant monomer–polymer interactions. Similar association is also expected when an anionic micelle adsorbs onto the polymer coil, like the one explained by Goddard [4] in the case of Necklace model. The hydrophobic contribution to the surfactant-polymer association arises from the interactions between the PEO chain and micellar aggregates in which a part of the polymer chain penetrates into the aggregates. On the whole, it can be said that hydrophilic–lipophilic balance between the surfactant and polymer moieties plays a governing role in the overall surfactant–polymer interactions.

Surfactant–polymer interactions become much more interesting from the fundamental point of view when, instead of single surfactant monomers or micelles, binary surfactants monomers or mixed micelles are involved [7, 8, 9, 10]. The unique properties of mixed micelles–polymer aggregates are also of considerable importance in the cosmetic industry [1d] where water-soluble polymers have been used in abundance. To meet this end, we have selected a combination of anionic surfactants such as SDS and SDBS and studied their mixed micelle formation in the presence of water-soluble polymers such as TBP, HPC, and CMC. The purpose of choosing SDS and SDBS was mainly their versatile applications in the cosmetic industry along with a variety of polyglycol derivatives [1d]. HPC, CMC, and their derivatives have been frequently used in the food industry along with some emulsifiers of anionic nature [11]. Therefore, it is expected that such a fundamental study of anionic mixed micelles with water-soluble polymers will pave the way for better understanding the surfactant–polymer interactions, both from the fundamental as well as industrial points of view.

In view of the complexities of these systems, we have preferred to study them with the help of various physiochemical techniques such as conductivity, fluorescence, cyclic voltammetry, and viscosity, which are considered to be quite sensitive to surfactant–polymer interactions. Conductivity and cyclic voltammetry will explain the behavior of charged aggregated species and their environments. Pyrene fluorescence is expected to throw light on the course of aggregation process predominantly due to hydrophobic interactions. Viscosity will demonstrate the viscoelastic nature of surfactant-polymer aggregates which should be different for different polymers.

Experimental

Materials

Sodium dodecyl sulfate (SDS), 99%, and sodium dodecyl benzene sulfonate (SDBS), 85% pure from Flüka, were repeatedly purified from ethanol and n-hexane, respectively, before use. Hydroxypropylcellulose (HPC), average molecular weight 100 000, carboxymethylcellulose sodium salt (CMC), average molecular weight 40 000, both from TCI, Japan, and triblock polymer (TBP), (polyethylene oxide)$_{27}$-(polypropylene oxide)$_{39}$-(polyethylene oxide)$_{27}$, average molecular weight 4600 (common name synperonic 85), cetylpyridinium chloride, and pyrene, from Flüka, were used as received. Potassium ferricyanide and potassium chloride were of AR Grade. 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 mixed micelle formation was studied in the presence of 0.001, 0.01, 0.1 w/v% TBP, 0.025 and 0.05 w/v% HPC and CMC. An automatic thermostat bath from Shimadzu, Japan, was used for maintaining the temperature within uncertainties of ± 0.05 °C. All measurements were performed at 25 °C.

Conductometric measurements

The conductivity measurements of SDS + SDBS mixtures in pure water, as well as in the presence of water-soluble polymers, were carried out over the whole mixing range with the help of digital conductivity meter (Model NDC-732) working at a fixed frequency of 1000 Hz manufactured by Naina Electronics, Chandigarh, India. A dip type conductivity cell with double-walled jacket to circulate the thermostated water was used for all measurements. The capacity of the conductivity cell was about 100 mL. The error in the conductance measurements was $\pm 0.5\%$.

Fluorescence measurements

The steady state pyrene fluorescence measurements were carried out with the help of a Perkin Elmer Spectrofluorometer (Model LS 50 B) at excitation wavelength of 335 nm. The concentration of pyrene used in all the measurements was approximately equal to 10^{-6} mol dm^{-3}. The ratio of the intensity of the pyrene emission, i.e., I_1/I_3 at 373 and 383 nm, respectively, was used in evaluating the polarity of environment in which pyrene was solubilized.

Cyclic voltammetric measurements

Cyclic votammetric experiments were performed using an Autolab Type II Electrochemical System (Ecochemie, Utrecht,

The Netherlands) equipped with PGSTAT 20 and driven by GPES software. The working electrode was highly polished glassy carbon electrode (GCE), having diameter 2 mm, and a platinum electrode used as counter electrode. The reference electrode was saturated Ag/AgCl electrode with a salt bridge containing 3 M KCl aqueous solution. The GCE surface was polished with aqueous slurry of alumina powder before each measurement. Pure nitrogen of purity 99.99% was used for the removal of oxygen from cell solution. In the present experiments, $K_3Fe(CN)_6$ was used as redox active electrochemical probe and KCl was used as supporting electrolyte.

Viscometric measurements

The efflux times of dilute solutions of single and mixed surfactants in pure water and in the presence of wate- soluble polymers were determined with the help of Ubbelohde type suspended level capillary viscometer sealed in a glass jacket to circulate the thermostated water at 25 °C. The time of flow for water was 175 s. This efflux time was kept long to minimize the need for applying the kinetic corrections to the observed data. Each experiment was carried out after giving long-time thermal stability and repeated at least twice in order to get reproducible results. A good reproducibility can be obtained by properly cleaning the viscometer with the help of concentrated chromic acid each time before starting a set of experiments and to avoid the formation of air bubbles inside the viscometer. From the ratio of efflux times of the test solution (t) to that of reference solution (t_o), the relative viscosity can be calculated ($\eta_{rel} = t/t_o$) by ignoring the density corrections for dilute solutions [1b, 12]. The measured η_{rel} were accurate to 0.5%, while the precision of these measurements was noted to be 0.2%.

Results and discussion

Conductivity and fluorescence behaviors

Collective representative conductivity (κ) plots of SDS + SDBS mixtures in pure water at some selected mole fractions have been shown in Fig. 1. Similar plots were also obtained in the presence of TBP, HPC, and CMC (not shown). It can be seen that each κ curve is very well separated by two linear portions and, therefore, a linear fitting procedure in each case, with
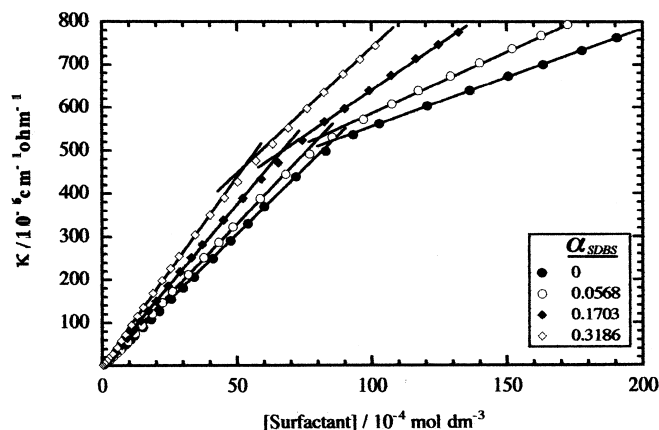
correlation factor always better than 0.999, can be used for evaluating critical micelle concentration (cmc) [13].

$$K_{pre} = K_o + S_{pre}\, Conc \tag{1}$$

$$K_{pre} = K_o' + S_{pre}\, Conc \tag{2}$$

Here, κ_o, κ_o' are the intercepts and S_{pre}, S_{post} are the slopes of the pre- and the post-micellar regions, respectively. The cmc values were calculated by equating Eqs. 1 and 2 as an unknown variable (conc). At certain mole fractions, where sharp breaks were not observed, the cmc values were computed from differential conductivity plots [14] (not shown). At some selected mole fractions, the cmc values were also determined from the variation of ratio of first to the third vibronic peaks [14b] (I_1/I_3) of pyrene with respect to an increase in the concentration (Fig. 2). A significant decrease in I_1/I_3 values
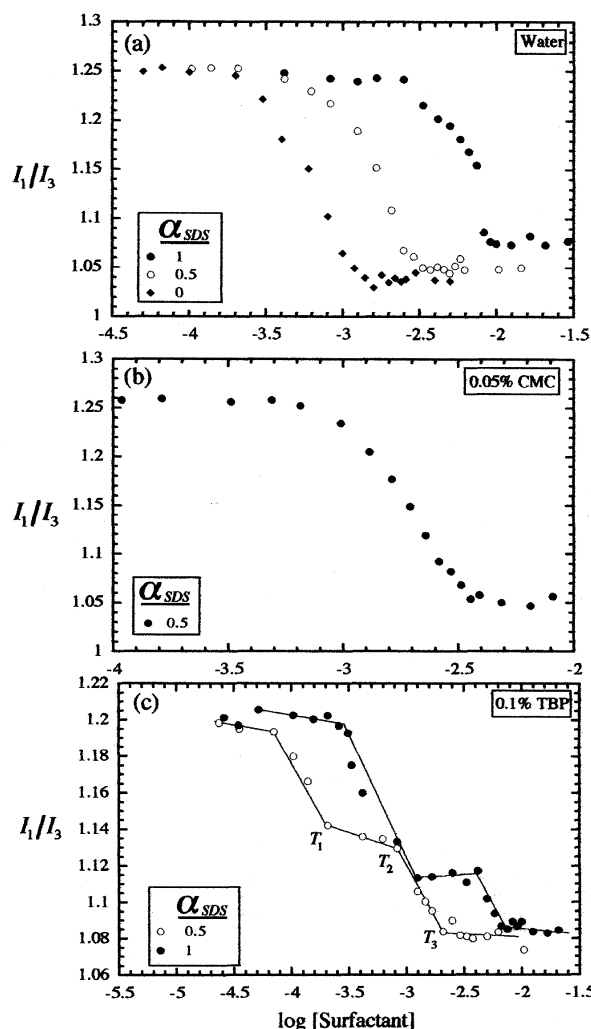

Fig. 1 Plot of conductivity (κ) versus [surfactant] of mixed SDS + SDBS mixtures at some selected mole fractions

Fig. 2a–c Plot of fluorescence intensity (I_1/I_3) versus log of [surfactant] for SDS + SDBS mixture in **a** pure water, **b** aqueous CMC, and **c** aqueous TBP

with an increase in the amount of single or mixed surfactants shows an aggregation process during which the aggregates grow in size and acquire a definite aggregation number which increase with the total concentration [14b] (Figs. 2a and b). The end of reversed sigmoidal curve gives the value of cmc. Figures 1 and 2a show a single aggregation process of mixed micelle formation by SDS + SDBS mixtures in pure water. Single aggregation process was also observed in the presence of HPC (not shown) and CMC (Fig. 2b). A significant difference between the conductivity and fluorescence behaviors has been observed in the presence of TPB. Figure 2c shows triple breaks (i.e., T_1, T_2, and T_3) in I_1/I_3 curve, indicating the presence of two kinds of aggregation processes whereas this is not so in the case of conductivity measurements (not shown). This behavior can be explained as follows: below T_1, free surfactant and polymer macromolecules exist and at T_1, the adsorption of surfactant monomers starts on the polymer backbone. The adsorption process goes on till the arrival of T_2 where the whole of polymer is occupied by the surfactant monomers and this point is termed the polymer saturation point (psp). From T_1 to T_2 the concentration of free surfactant monomers is expected to remain constant. After this, the conventional micelle formation process starts and completes at T_3, therefore, T_3 can be equated with conventional cmc. Similar behavior has also been reported for PEO-SDS [15] and PPO–SDS [16] systems. The T_1, T_2, and T_3 values at some mole fractions are listed in Table 1. Since no triple breaks were observed in 0.001% TBP, therefore, micelle formation is denoted by cmc. It would be appropriate if we compare T_3 value in the presence of 0.01 and 0.1% TBP with cmc in the presence of 0.001% TBP. A comparison among T_3 and cmc values (Table 1) indicates that especially in the case of pure SDS and SDBS, first the cmc increases and then subsequently decreases with the increase in the amount of TBP. For SDS, T_3 is much lower in the presence of 0.1% TBP than the cmc in pure water, whereas they are close to each other for SDBS. The situation becomes more intriguing in the case of $\alpha_{SDBS} = 0.5$, where the relative sequence of comparison observed in the case of pure SDS and SDBS is disturbed due to the compensating effects of both surfactants.

Initial increase in the cmc of both SDS and SDBS indicates that micelles become destabilized at 0.001% TBP, whereas a further increase in the TBP concentration results in the decrease in T_3. The former effect is most probably due to the lower probability of finding polymer macromolecules for surfactant–polymer interactions since the concentration of TBP is already very low in the solution. Therefore, it is expected that most of the TBP is available in the bulk and may be responsible for the medium effects which reduce the relative permittivity (ϵ) of the medium and thus produce a destabilizing effect on micelle formation [9a, b]. Consequently, a further increase in the concentration of TBP results in the higher probability of finding TBP macromolecules in the bulk, thus creating favorable opportunities for the adsorption of anionic surfactant monomers on the TBP backbone. This point can be argued on the basis of the fact that the adsorption of cationic Na^+ counterions on polymeric glycol, due to electrostatic interactions, imparts electropositive character to the glycol and hence facilitates its electrostatic interactions with anionic surfactant. Thus, TBP macromolecules saturated with surfactant monomers are expected to participate in the micelle formation along with the surfactant monomers. This will help in the reduction of T_3. However, this effect is much more pronounced in the case of SDS rather than SDBS and the difference is accounted for by stronger DS^- surfactant ion interactions than DBS^- with TBP in view of latter's bulky polar head group, which may create steric hindrance in the course of electrostatic interactions. Nagarajan [17] from his geometric model, has suggested that although the penetration of polymer segments at the interfacial region of the micelle induces a decrease in the interfacial free energy, it also increases the steric repulsion at the micellar interface.

Another quantitative micellar parameter that is directly related to synergism is the miceller aggregation number, N_{agg}, i.e., the minimum number of like or unlike monomers required for single or mixed micelle formation. The value of N_{agg} can be evaluated from the fluorescence data. The solubilization of pyrene in the interior of the micelle is frequently described by the Poisson distribution model and is explained on the basis

Table 1 Values of T_1, T_2, $T_{2,vis}$, T_3, and cmc$\times10^{-4}$ mol dm^{-3} for SDS + SDBS in aqueous 0.1, 0.01, and 0.001% TBP and in pure water

	0.1% TBP				0.01% TBP			0.001% TBP	0.0% TBP		
	T_1	T_2	$T_{2,vis}$	T_3	T_1	T_2	T_3	cmc	cmc$_{Fl}$	cmc$_{Vis}$	cmc$_\kappa$
SDS	10	30	32	71	25	63	87	89	85 (80) [30]	85	85 (80) [24a]
SDBS	4.0	11	–	14	1.0	3.0	31	40	16	30	22
$\alpha_{SDS} = 0.5$	2.0	7.9	8.0	20	6.0	14	60	41	30	–	35

cmc$_{Fl}$, cmc$_{Vis}$, and cmc$_\kappa$ from fluorescence, viscosity, and conductivity measurements, respectively. Values in parentheses are literature values

of Poisson statistics [14b, 18]. The N_{agg} can be determined by measuring the intensity of fluorescence probe with and without quencher (Q), I and I_o, respectively, and is given by the following equation:

$$I = I_o \exp\left(-\frac{[Q]}{[M]}\right) \qquad (3)$$

where [M] is the concentration of single and mixed micelles and is related to N_{agg} as follows

$$[M] = \left(\frac{[surf]_{total}-[surf]_{free}}{N_{agg}}\right) \qquad (4)$$

where $[surf]_{total}$ is the total concentration of single or mixed surfactants and $[surf]_{free}$ is the concentration of surfactant monomers which can be easily equated with the cmc value. Thus, combining Eqs. 3 and 4 will yield the following equation:

$$\ln\left(\frac{I_o}{I}\right) = \frac{[Q]N_{agg}}{[surf]_{total}-cmc} \qquad (5)$$

In the present study, cetylpyridinium chloride was used as quencher. The N_{agg} values for SDS, SDBS, and at equimolar proportion in pure water as well as in the presence of various polymers have been determined and listed in Table 2. It can be seen that N_{agg} values for SDS in the presence of different polymers are higher than in pure water, whereas the reverse is true for SDBS. The N_{agg} value of SDS + SDBS mixture indicates a compensating effect of both SDS and SDBS. A higher N_{agg} value for SDS in the presence of different polymers may indicate the participation of polymer macromolecules in the micelle formation process of SDS. The largest N_{agg} value in the presence of CMC can be attributed to the further stabilization of SDS–CMC micellar aggregates due to the adsorption of additional Na^+ counterions at the micelle solution interface, which is perhaps not possible in the presence of TBP and HPC. The additional Na^+ counterions are provided by the dissociation of CMC anionic polyelectrolyte in aqueous solution. However, it is to be mentioned that single aggregation process was observed for SDS in the presence of HPC and CMC and, hence, the mode of interactions between SDS and TBP macromolecules is different from that of

SDS with HPC or CMC. Although both HPC and CMC are cellulose derivatives and the former is neutral whereas the later is an anionic polyelectrolyte, both are expected to have similar kind of interactions with SDS. Since CMC is not expected to interact electrostatically with DS^- monomers due to their identical polarities, nor does HPC, the probability of adsorption of SDS monomers on the HPC or CMC backbone diminishes with the result that no additional break is observed before the actual cmc. Recalling a general trend in N_{agg}, one would find that N_{agg} value decreases in the case of SDS + PEO [19], SDS + PVA [19d], and SDS + PVP [19b–d], whereas in certain cases viz. SDS + alcohols [20], SDS + alkanes [20], and octyl β-D-thioglucopyranoside + PPO [6], N_{agg} value increases in comparison to that in pure water. This trend is generally correlated to the mode of association of polymers with micelles. Consequently, if polymer penetrates into the micelle, or in other words if it participates in the micelle formation, N_{agg} value increases during the solubilization of long-chain alcohols or alkanes into the interior of the micelle [20]. On the contrary, a decrease in N_{agg} value, as in the case of SDBS, suggests that polymer macromolecules do not participate in the micelle formation process, most probably due to the steric hindrances created by bulky aromatic head groups [17]. It means that SDBS micelles adsorbed on the polymer backbone may not be fully stabilized by this association. This is also evident from a value of T_3 slightly lower than cmc in the presence of TBP (Table 1). However, one cannot completely exclude the possibility of SDBS + TBP interactions since the triple break in Fig. 2c is clear experimental evidence of aggregate formation, which may not participate in the independent micelle formation process of SDBS.

## Cyclic voltammetric behavior

From cyclic voltammetric measurements, the diffusion coefficient (D) of electroactive probe (ferricyanide ion) was evaluated in aqueous micellar solution [21] of SDS, SDBS, and their mixture in the absence as well as in the presence of TBP, HPC, and CMC, in order to compare it with N_{agg}. Figure 3a shows typical cyclic voltammo-

Table 2 Values of N_{agg} and $D \times 10^{-6}$ cm^2/s of ferricyanide ion for SDS, SDBS, and SDS + SDBS mixture in pure water and in the presence of polymers

	Pure water		0.1% TBP		0.05% HPC		0.05% CMC	
	N_{agg}	D	N_{agg}	D	N_{agg}	D	N_{agg}	D
SDS	63 ± 3	5.1 ± 0.3	98 ± 4	0.8 ± 0.03	82 ± 3	9.9 ± 0.4	110 ± 4	17 ± 0.4
	(63 ± 3)							
SDBS	67 ± 3	3.8 ± 0.4	42 ± 3	3.9 ± 0.3	41 ± 2	6.3 ± 0.1	55 ± 2	2.1 ± 0.02
$\alpha_{SDS} = 0.5$	70 ± 2	1.9 ± 0.2	69 ± 3	3.6 ± 0.4	59 ± 3	7.4 ± 0.3	79 ± 3	12 ± 0.3

Value in parentheses is the literature value

Fig. 3 a Cyclic voltammograms of ferricyanide ion in 0.016 mol dm^{-3} aqueous SDS solution containing 0.1 mol dm^{-3} KCl at various scan rates. b Plot of i_{pa} (μA) versus $s^{1/2}$ (V/s)$^{1/2}$ for ferricyanide ion in aqueous surfactant solution in the absence and presence of water-soluble polymers
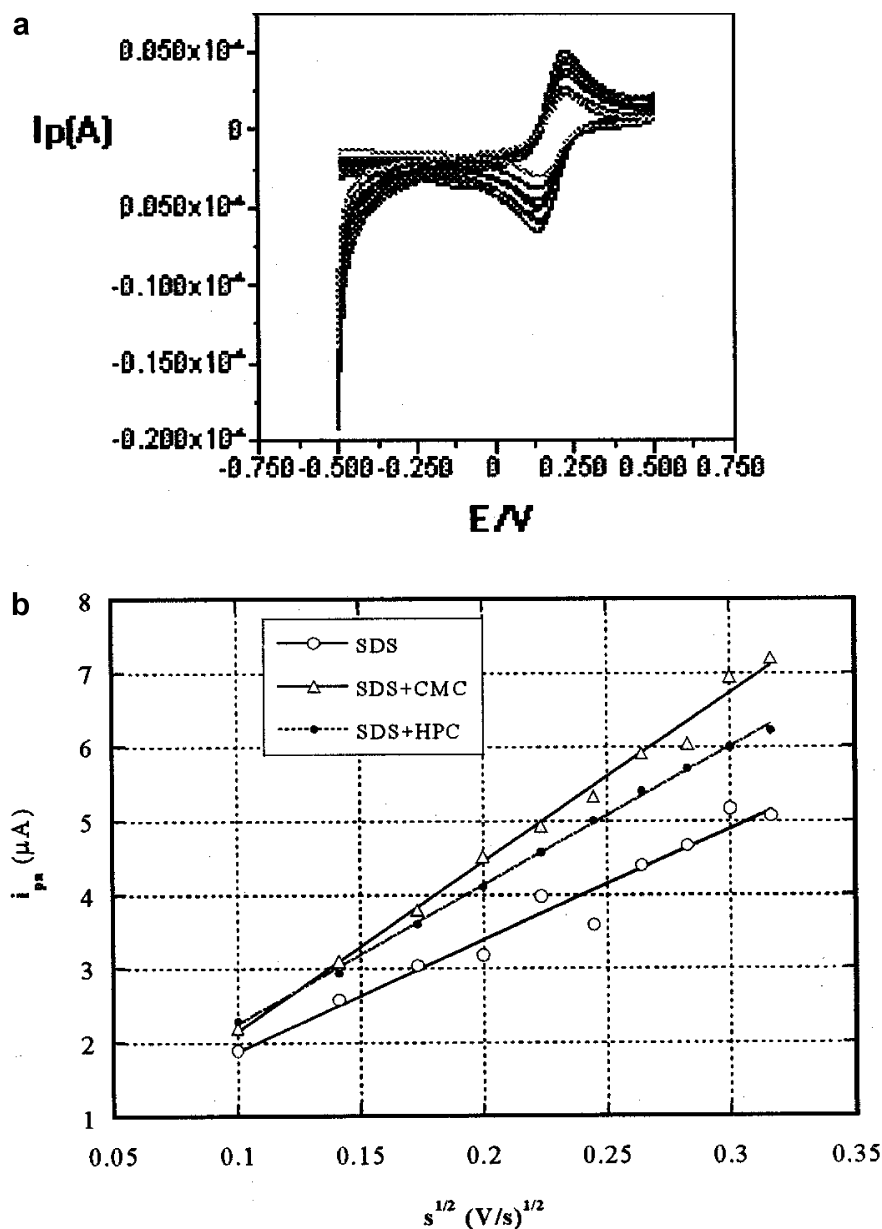
grams of ferricyanide ion in aqueous 0.016 mol dm^{-3} SDS and 0.1 mol dm^{-3} KCl as swamping electrolyte at various scan rates (10 to 100 mV/s). It represents one electron reversible step in aqueous micellar solution and which is evident from the ratio of anodic to cathodic peak currents (i_{pa}/i_{pc})≈1. Furthermore, the separation between the anodic and cathodic peak potentials, ΔE_p, for ferricyanide ion in aqueous micellar solutions was found to be 60–70 mV. The value of anodic peak current, i_{pa}, for one electron reversible process is related to D of electroactive probe by the Randels-Sevcik equation [22] in the following form

$$i_{pa} = 0.4463FAC(F/RT)^{1/2}s^{1/2}D^{1/2} \qquad (6)$$

where A is the area of electrode, s is the scan rate, and all other parameters have their usual meanings. Figure 3b shows the plot of i_{pa} versus $s^{1/2}$ for electroactive probe in 0.016 mol dm^{-3} SDS aqueous micellar solution in the absence and presence of water-soluble polymers. Similar plots were also obtained in aqueous SDBS and SDS + SDBS micellar solutions (not shown). All plots show linear variation and from the slopes of these plots, D can be evaluated. The values of D thus obtained are listed in Table 2.

Interestingly, D values show quite compatible behavior to that of N_{agg}. In the case of SDS, D values are higher in the presence of all water-soluble polymers (except 0.1% TBP) than in pure water and highest in the

presence of CMC. A high D value indicates that electroactive probe can easily diffuse through a solution consisting of micellar aggregates, whereas a low D value demonstrates the entrapment of electroactive probe by compact micellar aggregates. One would always expect loose SDS–CMC aggregates in comparison to pure SDS micelles on the basis of head group repulsions pertaining to the identical anionic character of both SDS and CMC, which should be much more pronounced for SDS–CMC micellar aggregates than for pure SDS micelles. On the contrary, in the presence of 0.1% TBP, the D value is much smaller than in pure water. Such a small D value indicates that the diffusion of electroactive probe is significantly hindered through SDS–TBP aggregates, which are even much more stable and compact than pure SDS micelles since the T_3 value is much smaller than cmc of SDS in pure water (Table 1). Furthermore, D value in the SDBS micellar solution in the presence of 0.1% TBP is not very much different from that in the absence of TBP, but is higher and lower in the presence of 0.05% HPC and CMC, respectively. A lower value in the presence of CMC is exactly opposite to that in the case of SDS and can be attributed to the further stabilization of CMC-free SDBS pure micelles, which is probably due to the adsorption of excess of Na$^+$ counterions. The D value of SDS + SDBS mixture again shows compensating effects between SDS and SDBS.

Micelle formation in the presence of water-soluble polymers

The cmc values of SDS + SDBS mixtures in pure water and in the presence of polymers, from κ measurements, are plotted in Fig. 4. These values for pure surfactants in water from different studies are listed in Table 1 and compared with those available in the literature. Ideal mixing is expected since both SDS and SDBS are anionic surfactants, thus, the interactions between unlike surfactant monomers in mixed micelles are considered to be similar to those of homomicelles [23a]. Hence, the activity coefficients should be taken as unity. This behavior can be evaluated by using a pseudo-phase thermodynamic model [23] which relates the ideal mixed cmc (cmc*) with the experimental cmc of the pure components by using the following equation in the case of ideal mixing,

$$\frac{1}{cmc^*} = \frac{\alpha_1}{cmc_1} + \frac{(1 - \alpha_1)}{cmc_2} \tag{7}$$

where α_1 is the mole fraction of surfactant 1 (SDS) in total mixed solute, and cmc$_1$ and cmc$_2$ are the values of pure component SDS and SDBS, respectively. The cmc* values thus calculated using Eq. 7 have also been shown in Figs. 4a and b. A comparison between the experimental mixed cmc and cmc* values in the case of pure
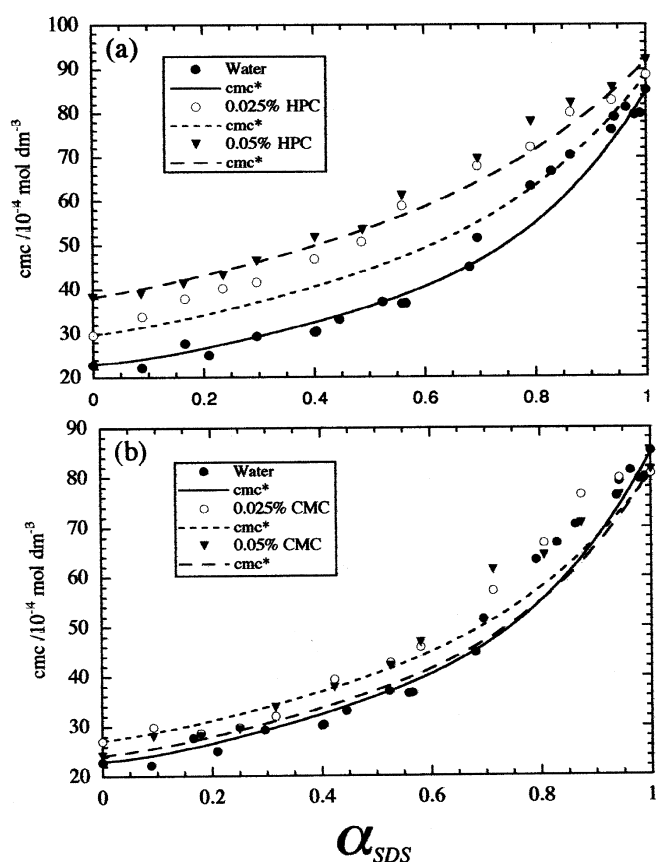

Fig. 4a–b Plot of cmc versus α_{SDS} for SDS + SDBS mixture in pure water and in **a** aqueous HPC and **b** CMC. Experimental cmc (*points*), predicted cmc* (*solid line*)

water predicts that cmc values show somewhat positive deviation from cmc* values, especially in the SDS rich region of the mixture. Similar behavior can also be observed in the presence of HPC and CMC. However, the cmc value shows a significant increase with the increase in the amount of HPC, whereas it remains more or less the same with increasing amounts of CMC.

In order to evaluate these results further on the basis of quantitative analysis, the non-ideal mixing behavior was computed by applying the regular solution (RS) formulation [23b]. The micellar mole fraction of SDS (x_1) and the interaction parameter (β) can be computed from the following Eqs. 8 and 9, respectively.

$$\frac{x_1^2 \ln(cmc\ \alpha_1 / cmc_1 x_1)}{(1 - x_1)^2 \ln(cmc(1 - \alpha_1) / cmc_2(1 - x_1))} = 1 \tag{8}$$

$$\beta = \frac{\ln\left(\frac{cmc\ \alpha_1}{cmc_1 x_1}\right)}{(1 - x_1)^2} \tag{9}$$

The β value is a measure of interactions between the two surfactants which lead to the deviations from the ideal behavior. Figure 5a demonstrates a graphical
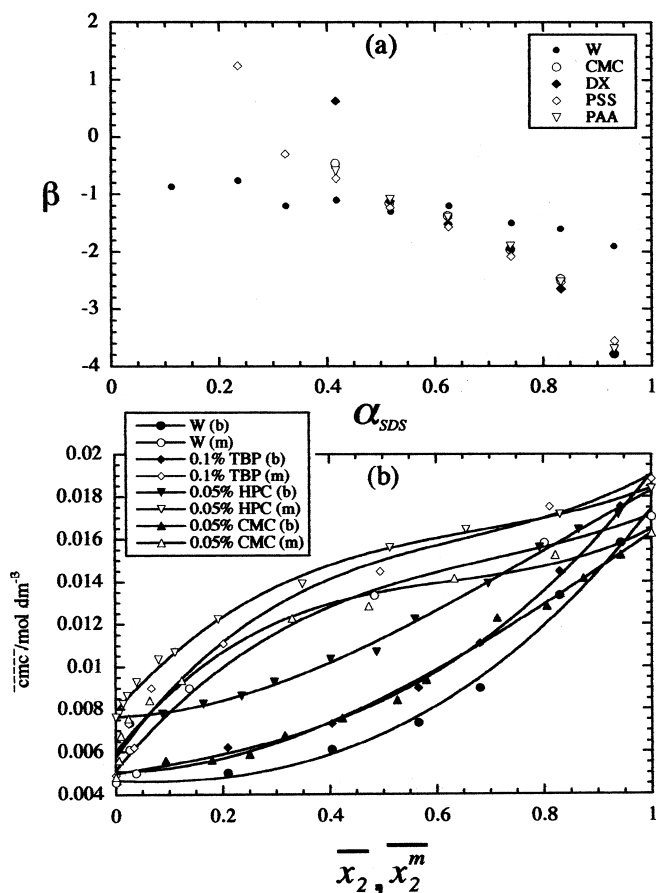
Fig. 5 a Plot of β versus α_{SDS} for SDS + SDBS mixture in pure water and in aqueous polymer. **b** Plot of $\overline{cmc}$ versus $\overline{x_2}$ (bulk mole fraction, *filled symbols*), and $\overline{x_2^m}$ (micelle mole fraction, *empty symbols*) in pure water and in aqueous polymer. In the *caption*, b and m represent bulk and micellar phases, respectively

presentation of β values for SDS + SDBS in pure water as well as in the presence of TBP, HPC, and CMC. The β value in pure water shows a quite strange variation from negative to positive value. However, it is to be mentioned here that within the framework of regular solution approximation [23b], β should be constant and should be close to zero in the case of structurally similar binary mixtures, which generally show ideal mixing. Interestingly, similar variation in β from negative to positive value has already been reported in the case of sodium hexyl sulfate + sodium decyl sulfate [24a] and hexyl trimethyl ammnoium bromide + alkyltrimethyl ammonium bromide mixtures [24b]. It seems that this approximation does not work properly for these systems. This problem has been discussed by Motomura et al. [25a], Puvvada et al. [25b], and Haque et al. [25c] in detail. Consequently, in the presence of TBP, HPC, and CMC, the β value becomes positive over the whole mole fraction range and the average β values are 1.1, 0.59, and 1.2, respectively. These positive values are, of course, not

so significant as to demonstrate a clear antagonistic behavior, hence the mixing behavior of SDS + SDBS in the presence of present polymers remains close to ideal.

In order to evaluate the present results further, the formulation proposed by Motomura and Aratono [26a], based on excess thermodynamic quantities, has been applied, which also takes into consideration dissociation of surfactant electrolyte. The details of this formulation have been given elsewhere [26b]. The composition of the mixed micelle can be determined by using the following equations:

$$\overline{x_2^m} = \overline{x_2} - (\overline{x_1}\,\alpha_2/\overline{cmc})(\partial\overline{cmc}/\partial\overline{x_2})_{T,P} \tag{10}$$

and

$$\overline{cmc} = (v_1x_1 + v_2x_2)\,\text{cmc} \tag{11}$$

where $\overline{x_2^m}$ is the micelle mole fraction and $\overline{x_2}$ is the bulk mole fraction of SDS in SDS + SDBS mixtures. $\overline{x_2}$ is given by

$$\overline{x_2} = v_2\alpha_2/(v_1\alpha_1 + v_2\alpha_2) \tag{12}$$

where v_1 and v_2 are the number of ions produced by the surfactant upon dissociation. Since each present surfactant is 1:1 electrolyte, two ions (i.e. anion and cation) are produced upon dissociation. Thus, v_1 and v_2 are given by $v_1 = v_{1,a} + v_{1,c}$ and $v_2 = v_{2,a} + v_{2,c}$ and hence, $\overline{cmc} = 2$ cmc.

The $\overline{x_2}$ and $\overline{x_2^m}$ values thus computed are plotted against $\overline{cmc}$ in Fig. 5b. This figure can be regarded as a phase diagram that represents the equilibrium of micelles with aqueous solution. The curves in pure water as well as in the presence of TBP, HPC, and CMC are more or less identical and show typical cigar-like behavior of ideal mixing [26a]. This demonstrates that the mixing behavior of SDS + SDBS mixtures remains more or less close to ideal, even in the presence of different water-soluble polymers. Similar results have already been reported by Liu et al. for tetradecyl pyridinium chloride (TeP) + decylammonium chloride (DeA) + sodium poly(L-glutamate) [8a] and TeP + DeA + sodium poly(2-acrylamide-2-methylpropane sulfonate) [8b] even though the mixed micelles of such combinations have significant interactions with these polymers.

Viscometric behavior

In order to further explore the mixed micelle–water-soluble polymer interactions, we carried out viscometric studies, which also demonstrate the mixing behavior of SDS + SDBS mixed micelles in the absence as well as in the presence of polymers. The relative viscosities (η_{rel}) of SDS + SDBS mixtures at the same concentrations (i.e less than 0.03 M) and mole fractions, which were used for the conductivity measurements, are presented in Fig. 6a. It can be seen that η_{rel} value more or less
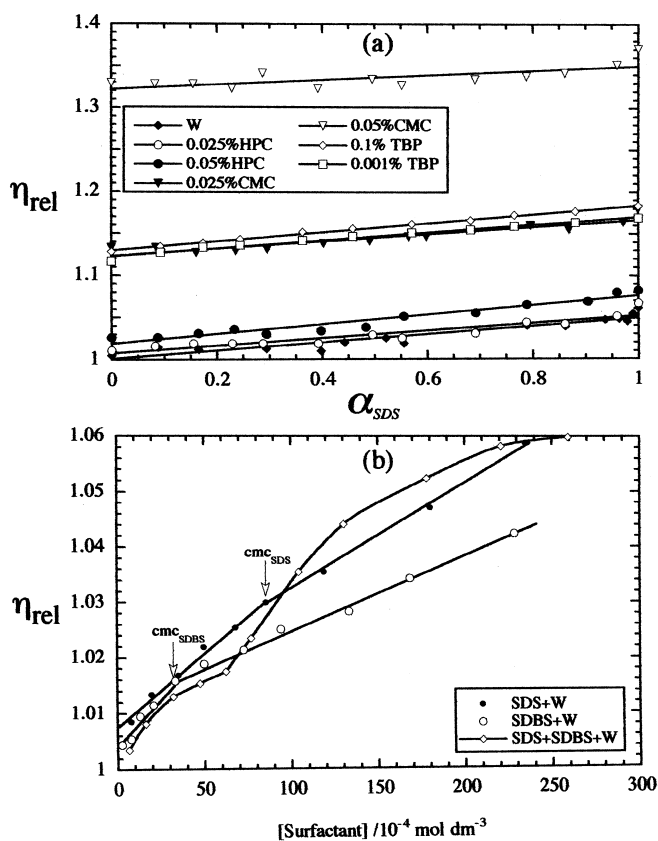
Fig. 6 a Plot of η_{rel} versus α_{SDS} for SDS + SDBS mixture in pure water and in aqueous polymer. **b** Plot of η_{rel} versus [surfactant] for SDS, SDBS, and their mixture ($\alpha_{SDS} = 0.5$) in pure water

satisfies the additivity rule over the whole mole fraction range, which means that the SDS + SDBS mixture is close to ideal in all cases. Furthermore, η_{rel} values increase with the increase in the amount of CMC, whereas they remain close to those in pure water in the presence of HPC over the whole mixing range. Since CMC, unlike HPC, is an anionic polyeletrolyte, upon dissolution in water it produces excess Na$^+$ cations, which are expected to further stabilize the SDS + SDBS mixed micelles by adsorbing at the mixed micelle–solution interface. Therefore, the presence of excess Na$^+$ counterions at the micelle–solution interface creates partial positive potential at the surface of the mixed micelles, which will have significant electrostriction effects in aqueous dipolar electrostatic environment. Such effects would be stronger at higher CMC concentration and thus produce greater viscous drag with the result that η_{rel} should increase [27] in the presence of CMC. Electrostriction effects are obviously not expected in the presence of neutral HPC polymer, therefore, η_{rel} remains more or less close to that in pure water. Intermediate electrostriction effects are expected in the presence of TBP due to the adsorption of both SDS and SDBS monomers on TBP backbone, which will result in an
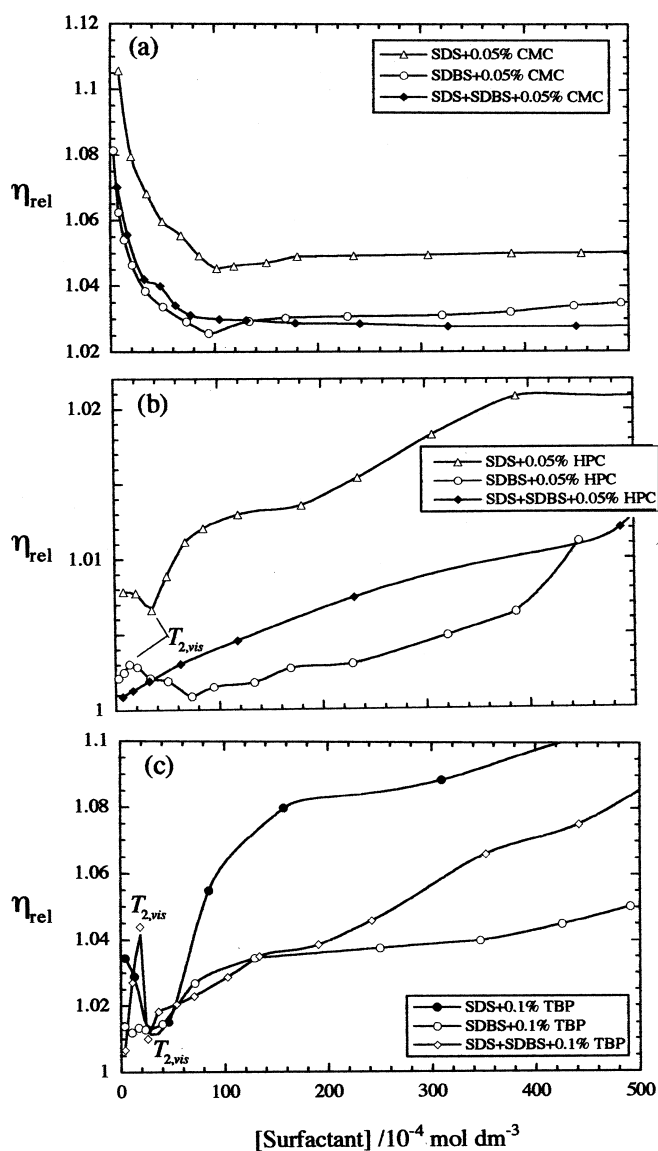

Fig. 7 Plot of η_{rel} versus [surfactant] for SDS, SDBS, and their mixture ($\alpha_{SDS} = 0.5$) in **a** aqueous CMC, **b** aqueous HPC, and **c** aqueous TBP

increase in the η_{rel} to above that in pure water but less than in the presence of CMC.

Viscosity measurements have also been performed to evaluate the micelle formation of SDS, SDBS, and their mixture. Figure 6b shows the plots of η_{rel} of single and mixed micelle formation. The η_{rel} in all the cases increases with the increase in concentration and shows a clear break at the cmc (represented by arrows in Fig. 6b) in each case [28]. The cmc value for SDBS is higher than the value obtained from fluorescence and conductivity measurements. In the presence of water-soluble polymers, we preferred to plot relative viscosity rather than reduced viscosity as shown in Fig. 7. A plot of reduced viscosity suppressed the changes due to the concentration

effects, hence it was not possible to locate the cmc in a very dilute concentration range (not shown). Figures 7a, b, and c show η_{rel} for SDS, SDBS, and their mixture at equimolar proportions in the presence of CMC, HPC, and TBP, respectively. Figure 7a shows typical η_{rel} plots in aqueous polyelectrolyte solution in which first the η_{rel} value decreases instantaneously and then it levels off with the further increase in the concentration. This is a typical behavior of aqueous polyelectrolyte systems and is attributed to a change in the structure of water-soluble polyelectrolyte from a linear to a coil form [29] upon surfactant–polymer association. In the presence of HPC (Fig. 7b), however, typical polyelectrolyte behavior observed in Fig. 7a vanishes away and a typical micelle formation process as observed in pure water (Fig. 6b) appears. A clear minimum in SDS + HPC curve around 34 mol dm^{-3} represents the psp which is, of course, not observed either from conductivity or fluorescence measurements. Exactly similar behavior of SDS in aqueous poly(n-isopropylacrylamide) has been reported by Mylonas et al [30] from viscosity studies. On the contrary, the psp is represented by a small maximum around 15 mol dm^{-3} of SDBS in SDBS + HPC curve, whereas, SDS + SDBS equimolar mixture again demonstrate the compensating effects. The psp can also be observed for SDS in the presence of TBP (Fig. 7c), however, no psp is observed for SDBS. The SDS + SDBS mixture shows psp in the form of a strong maximum. The psp values ($T_{2,vis}$) thus computed are compared with T_2 obtained from the fluorescence measurements in Table 1 in the presence of 0.1% TBP. Both values are quite compatible with each other. Interestingly, at the constant amount of SDS, SDBS, or their equimolar mixtures (Fig. 8a), the addition of CMC leads to a significant increase in the η_{rel} in the case of SDS, which is most probably due to an increase in the electrostriction effects upon stronger SDS–CMC association. Addition of HPC demonstrates a clear cmc in the case of SDS, which is represented by a strong maximum (Fig. 8b). One would really wonder why cmc is demonstrated by a sharp maximum in Fig. 8b instead of a minimum in Fig. 7b in the case of SDS and vice versa in the case of SDBS. The former can be attributed to a favorable association between SDS micelles and HPC, which produces large aggregates with higher viscosity upon addition of HPC in aqueous micellar solution. The latter can be explained on the basis of the adsorption of SDS monomers on HPC backbone resulting in the diminishing of electrostriction effects. Addition of TBP in aqueous SDS shows a somewhat polyelectrolyte behavior due to the adsorption of SDS monomers on TBP backbone (Fig. 8c), whereas no such variation is observed in aqueous SDBS or SDS + SDBS mixture. Similar results have already been reported for SDS with other triblock polymers in the literature [31, 32].

On the whole, Figs. 7 and 8 demonstrate that either surfactant is added in aqueous polymer systems or vice
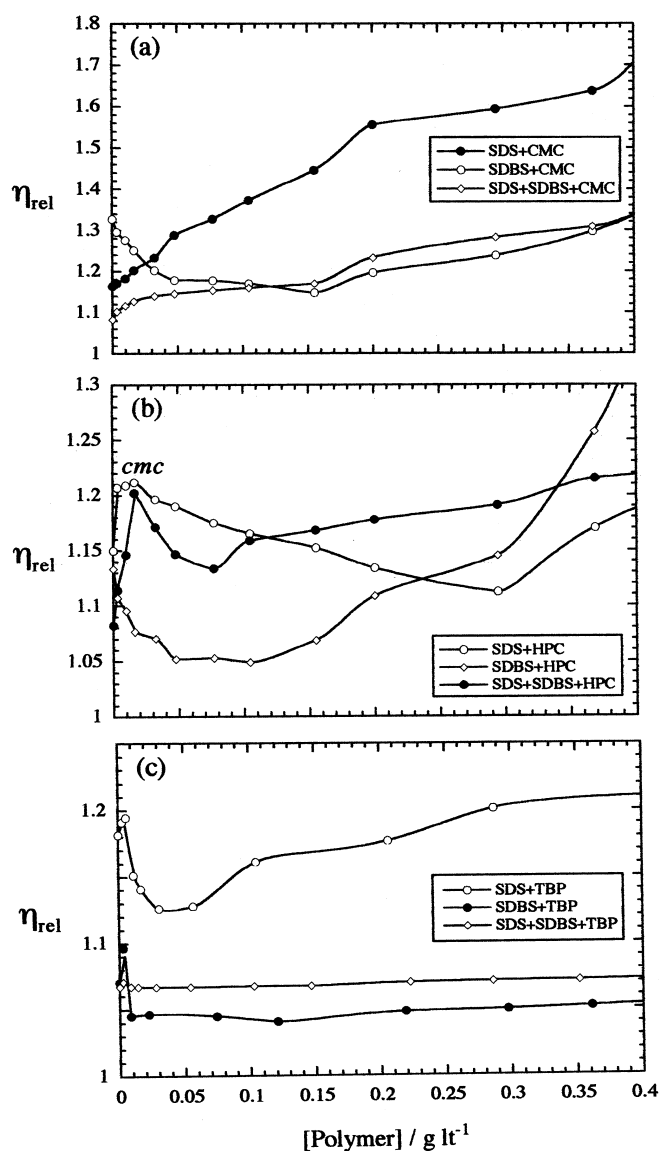

Fig. 8 a CMC, **b** HPC, and **c** TBP in aqueous SDS, SDBS, and their mixture ($\alpha_{SDS} = 0.5$)

versa, in both cases SDS has stronger interactions with all present water-soluble polymers than SDBS. Apart from this, even the mode of interactions between SDS and polymers seems to be almost opposite those between SDBS and polymers. This is mainly attributed to the presence of unfavorable steric factors operating in the latter case due to the presence of the aromatic bulky head group.

Conclusions

Anionic surfactant–polymer interactions have been studied for SDS, SDBS, and SDS + SDBS mixtures with

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TBP, HPC, and CMC. Fluorescence measurements showed clear cmc processes regarding the adsorption of SDS, SDBS, or SDS + SDBS monomers on the TBP backbone, which are much more significant and favorable in the case of SDS. Similarly, SDS has stronger association with CMC and HPC than SDBS. It has also been concluded that SDS–polymer aggregates also participate in actual micelle formation while no clear experimental evidence demonstrates such participation of SDBS–polymer aggregates in the micelle formation process of SDBS, due to the steric incompatibility of the aromatic head group of SDBS. The SDS + SDBS mixed surfactants–polymer interactions have been found to have compensating effects to those between the pure surfactants. The mixed micelle formation process in the absence and presence of all polymers was found to be ideal in nature.

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