Colloid Polym Sci (2002) 280: 990–1000
DOI 10.1007/s00396-002-0717-9

ORIGINAL CONTRIBUTION

Mandeep Singh Bakshi
Shweta Sachar
Nipun Mahajan
Ishpinder Kaur
Gurinder Kaur
Narpinder Singh
Pankaj Sehgal
Hidekazu Doe

Mixed-micelle formation by strongly interacting surfactant binary mixtures: effect of head-group modification

Received: 15 February 2002
Accepted: 15 April 2002

M.S. Bakshi (✉) · S. Sachar · N. Mahajan
I. Kaur
Department of Chemistry, Guru Nanak Dev University, Amritsar 143005, Punjab, India

G. Kaur
Department of Applied Physics,
Guru Nanak Dev University,
Amritsar 143005, Punjab, India

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

P. Sehgal · H. Doe
Department of Chemistry,
Faculty of Science, Osaka City University,
Sugimoto, Sumiyoshi-ku, Osaka 558, Japan

Abstract The mixing behavior of several cationic plus anionic surfactant binary mixtures, viz., sodium dodecyl benzene sulfonate (SDBS) plus hexadecyltrimethylammonium bromide (HTAB), SDBS plus tetradecyltrimethylammonium bromide (TTAB), SDBS plus tetradecyltriphenylphosphonium bromide (TTPB), sodium dodecyl sulfate (SDS) plus TTPB, SDBS plus hexadecylpyridinium chloride (HPyCl), and SDS plus HPyCl was studied in pure water with the help of conductivity, interfacial tension, turbidity, and viscosity measurements. The mixed-micelle formation was evaluated with the help of the Clint equation and the regular solution approximation. It was observed that head-group modification had a significant influence on the nature of the mixed-micelle formation. The SDBS plus TTAB mixed micelles showed positive departure from ideality and had positive values for the regular solution interaction parameter, β. The SDS plus HPyCl mixture showed both negative and positive departures in the SDS- and HPyCl-rich regions of the mixtures, respectively, from ideality. The SDBS + TTPB mixture remained close to ideal, and the SDBS plus HTAB, SDBS plus HPyCl, and SDS plus TTPB mixtures showed synergistic behavior. The positive β value in the case of the SDBS plus TTAB mixture was not the result of antagonistic behavior, but was due to the higher value of the mixed critical micelle concentration compared to the ideal mixed cmc values in the ideal state (obtained from the Clint equation) and which was the consequence of unavailability of unlike monomers in the formation of insoluble salt owing to the neutralization of the unlike monomers with opposite polarities. The SDBS plus HTAB mixture did not show similar behavior, most probably owing to the larger size and lower charge density at HTA^+ in comparison to at TTA^+, which could have resulted in the former having weaker electrostatic interactions with the DBS^- anion in comparison to the latter. The weaker electrostatic interactions in conjunction with the packing geometrical constraints are responsible for the close-to-ideal behavior of the SDBS plus TTPB mixture.

Keywords Strongly interacting surfactants · Mixed micelles · Bulky head groups · Turbidity

Introduction

A significant amount of research work has been devoted to understanding the physiochemical aspects of mixed-micelle formation by two or more surfactants [1, 2, 3]. These fundamental properties of such kinds of systems are of utmost importance in view of their appropriate industrial applications which pave the way to locate the most suited surfactant combinations with desired surface activities from application as well as economics points of view [4]. Mixed-micelle formation has considerable importance in comparison to single-surfactant micelle formation from various applied aspects. Generally, a mixture of two or more surfactants has better surface activity than any of the constituents [1, 2]. In the mixed-micelle process three possibilities exist, i.e., favorable interactions, unfavorable interactions, or ideal mixing between the monomers of two unlike surfactants. Favorable interactions have been demonstrated by mixtures of ionic–nonionic, ionic–zwitterionic, and cationic–anionic surfactant combinations [1, 2, 3, 4]. Among all these, cationic–anionic surfactant combinations experience the strongest favorable interactions owing to the strong electrostatic interactions between the oppositely charged polar head groups [5, 6, 7, 8, 9], which otherwise oppose the micelle formation. In comparison to all other combinations, strongly interacting surfactants have been least explored since they immediately undergo precipitation upon mixing; hence, they pose considerable experimental difficulties in order to explore their mixing behavior in the solution phase.

Although oppositely charged surfactant combinations are very important binary surfactant combinations with extraordinary micellar properties owing to their strong synergistic behavior, a comprehensive study dealing with the effect of head-group modifications directly related to their mixing behavior is still lacking. This is probably due to the appearance of phase separation upon mixing these surfactants. Some of the well-documented examples of strongly interacting surfactant combinations are sodium dodecyl sulfate (SDS) plus decyltrimethylammonium bromide [7], sodium dodecyl benzene sulfonate (SDBS) plus cetyltrimethylammonium tosylate [8], and SDS plus dodecylpyridinium chloride[10] mixtures, in which phase separation occurs over most of the mole fraction range. However, in view of such studies, it is also possible to reduce the degree of synergism in these systems by manipulating the nature of the strongly interacting surfactant head groups and thus reducing the chances of phase separation.

In the present study, the surfactant combinations were selected in such a way that the polar head groups of unlike monomers should have considerable influence on the compatibility of unlike monomers in the mixed state, for example, as in the case of SDBS plus hexadecyltrimethylammonium bromide (HTAB) mixtures, where apart from the presence of opposite polarity, incompatibility is also expected in the packing arrangement of unlike bulky polar head groups in the mixed state. This kind of incompatibility will certainly reduce the strong electrostatic interactions operating between the oppositely charged head groups owing to the screening effects and will thus minimize the chances of precipitation. Hence, the present study has two objectives; first, to evaluate the physiochemical properties of strongly interacting surfactant mixtures and, second, to study the influence of head-group modifications on the extent of mixed-micelle formation.

Experimental

SDBS and SDS were purchased from Aldrich and were used as received. HTAB, tetradecyltrimethylammonium bromide (TTAB), tetradecyltriphenylphosphonium bromide (TTPB), and hexadecylpyridinium chloride (HPyCl), from Lancaster Synthesis, UK, were recrystallized from acetone/2-propanol mixtures. Triply distilled conductivity water was used in the preparation of all the solutions. The solutions were prepared by mass with an accuracy of ±0.01 mg. The mole fractions were accurate to ±0.0001 units. All the measurements were performed at 25 °C.

Conductometric measurements

The conductivity measurements were carried out over the whole mixing range except in those cases where medium to intense cloudiness appeared. In order to study the salt effect, the mixed micellization of the SDBS plus TTAB mixtures was also carried out in aqueous 0.001 and 0.005 mol dm^{-3} NaBr. All the measurements were carried out with the help of a digital conductivity meter (model NDC-732) working at a fixed frequency of 1,000 Hz manufactured by Naina Electronics, Chandigarh, India. A dip-type conductivity cell with a double-walled jacket to circulate the thermostated water was used for all the measurements. The capacity of the conductivity cell was about 100 ml. An automatic thermostat bath from Shimadzu, Japan, was used for maintaining the temperature within uncertainties of ±0.05 °C. The error in the conductance measurements was ±0.5%.

Interfacial tension measurements

The interfacial behavior of the binary mixtures at some selected mole fractions where the conductivity curves did not show sharp breaks was studied with the help of a pendant-drop instrument equipped with and a charge-coupled device (CCD) camera (model PD-X, Kyowa Interface Science Co, Japan). A drop of sample was formed by using a syringe of 1 cm^3, which was fitted with a Teflon needle of 22 gauge. An image of the drop was formed by the CCD camera attached to the instrument. The instrument was calibrated with deionized water.

Turbidity measurements

The turbidity measurements for all the binary surfactant mixtures over the whole mole fraction range were performed using a Nephelo-Turbidity meter (type 131, Systronics, India) after allowing sufficient time for equilibration. This instrument works on the basis of the 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 photomultiplier tube which gives the turbidity of the solution in arbitrary nephelo turbidity units.

Viscometric measurements

The efflux times of dilute solutions of the mixed surfactant systems were determined with the help of a Ubbelohde-type suspended level capillary viscometer which was sealed in a glass jacket to circulate the thermostated water at 25 °C. The time of flow for the water was 175 s. This efflux time was kept long to minimize the need for applying kinetic corrections to the observed data. Each experiment was carried out after allowing long-time thermal stability to be reached and was repeated at least twice in order to get reproducible results. 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 to avoid the formation of air bubbles in the viscometer. From the ratio of the efflux times of the test solution, t, to that of the reference solution, t_0, the relative viscosity can be calculated, $\eta_r = t/t_0$ by ignoring the density corrections for the dilute solutions [8, 11].

Results and discussion

Conductivity behavior

Collective representative conductivity, κ, plots of the SDBS plus TTAB mixtures are shown in Fig. 1. Similar plots were obtained in the cases of SDBS plus HTAB, SDBS plus TTPB, SDS plus TTPB, SDBS plus HPyCl, and SDS plus HPyCl mixtures. Each plot showed a linear variation in the κ values with respect to an increase in the concentration of single as well as of mixed surfactants in both the premicellar and postmicellar regions. The slope in the premicellar region was always greater than that in the postmicellar region. The intersection point between the two straight lines gave the critical micelle concentration (cmc). The values for all the mixtures were calculated as explained earlier [12, 13] and are listed in Tables 1, 2, 3, and 4 along with their uncertainties. The cmc values for the pure components are compared with those already available in the literature and are found to be in good agreement with each other. It is to be noted in Fig. 1 that the break corresponding to the cmc is quite sharp in the case of pure TTAB, i.e., $\alpha_{TTAB} = 1$, but the sharpness decreases

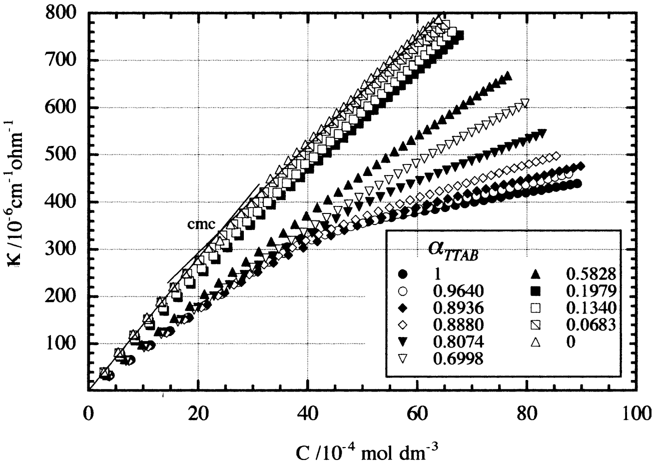

Fig. 1. Conductivity, κ, versus concentration, c, of the sodium dodecyl benzene sulfonate (*SDBS*) plus tetradecyltrimethylammonium bromide (*TTAB*) mixture in pure water at corresponding mole fractions of TTAB

Table 1. Values of the critical micelle concentration (cmc) and the ideal mixed cmc (*cmc**) 10^{-4} moldm^{-3} of strongly interacting surfactant mixtures in water. Sodium dodecyl benzene sulfonate (*SDBS*), hexadecyltrimethylammonium bromide (*HTAB*), tetradecyltrimethylammonium bromide (*TTAB*)

SDBS + HTAB			SDBS + TTAB		
α_{SDBS}	cmc	cmc*	α_{SDBS}	cmc	cmc*
0.000	9.53 ± 0.07 (9.2) [3] (10.0) [20]	9.53	0.000	37.9 ± 0.26 (38.0) [29]	37.9
0.1320	8.86 ± 0.18	10.3	0.0360	38.6 ± 0.49	37.0
0.2421	9.65 ± 0.27	11.1	0.1064	39.2 ± 0.42	35.4
0.3366	11.0 ± 0.72	11.8	0.1120	39.4 ± 0.64	35.3
0.4891	10.7 ± 0.70	13.3	0.1926	39.8 ± 0.79	33.6
0.6333	12.8 ± 1.1	15.1	0.3002	38.8 ± 1.7	31.6
0.7422	15.8[a]	16.8	0.4172	38.1 ± 2.3	29.7
0.8273	14.8[a]	18.4	0.8021	36.1[a]	24.7
0.8961	18.9 ± 1.5	19.9	0.8660	34.5[a]	24.1
0.9421	17.4[a]	21.1	0.9317	31.6[a]	23.4
0.9700	20.8 ± 1.3	21.9	1.000	22.8 ± 2.2	22.8
1.000	22.8 ± 2.0	22.8			

[a] cmc values evaluated from γ measurements

Table 2. Values of cmc and cmc*/10^{-4} moldm^{-3} of strongly interacting surfactant mixtures in water. Hexadecylpyridinium chloride (*HPyCl*), tetradecyltriphenylphosphonium bromide (*TTPB*)

SDBS + HPyCl			SDBS + TTPB		
α_{SDBS}	cmc	cmc*	α_{SDBS}	cmc	cmc*
0.000	10.1 ± 0.08 (10.0) [14]	10.1	0.000	8.18 ± 0.45	8.18
0.0777	10.0 ± 0.44	10.5	0.1120	8.48 ± 0.72	8.81
0.1190	9.83 ± 0.61	10.8	0.2100	9.45 ± 0.94	9.45
0.1510	9.71 ± 0.69	11.0	0.7992	16.6[a]	16.8
0.2202	9.38 ± 0.69	11.5	0.8781	17.8 ± 1.3	18.7
0.2220	9.56 ± 0.61	11.5	0.9053	18.5[a]	19.5
0.2857	10.5 ± 1.8	12.0	1.000	22.8 ± 1.6	22.8
0.3120	9.45 ± 0.65	12.2			
0.8847	17.0[a]	19.9			
0.9009	18.5 ± 1.1	20.3			
0.9352	18.1 ± 1.4	21.1			
0.9581	18.6[a]	21.7			
0.9682	20.4 ± 1.6	21.9			
0.9801	21.0 ± 1.6	22.2			
1.000	22.8 ± 1.8	22.8			

[a] cmc values evaluated from γ measurements

Table 3. Values of cmc and cmc*/10^{-4} moldm^{-3} of strongly interacting surfactant mixtures in water. Sodium dodecyl sulfate (*SDS*)

SDS + HPyCl			SDS + TTPB		
α_{SDS}	cmc	cmc*	α_{SDS}	cmc	cmc*
0.000	10.1 ± 0.32	10.1	0.000	9.64 ± 0.73	9.64
0.0362	10.7 ± 0.17	10.4	0.9178	49.0[a]	51.5
0.0731	11.1 ± 0.33	10.8	0.9527	61.1 ± 2.5	61.8
0.1093	12.3 ± 0.30	11.1	0.9641	68.0 ± 2.6	66.1
0.1429	13.1 ± 0.17	11.5	0.9745	69.3 ± 2.3	70.5
0.1770	14.1 ± 0.18	11.9	0.9839	67.6[a]	75.0
0.9625	54.9[a]	66.1	0.9992	72.9 ± 2.6	83.9
0.9763	60.6 ± 2.5	71.9	1.000	84.4 ± 4.0	84.4
0.9898	64.6[a]	78.6			
0.9905	63.0 ± 2.8	78.9			
0.9924	69.9 ± 11	79.9			
0.9939	69.3 ± 3.4	80.8			
0.9953	78.7 ± 2.2	81.6			
0.9968	80.4 ± 1.3	82.5			
0.9980	82.9 ± 2.4	83.2			
0.9992	83.8 ± 2.4	84.0			
1.000	84.4 ± 1.3 (80.0) [30]	84.4			

[a] cmc values evaluated from γ measurements

Table 4. Values of cmc and cmc*/10^{-4} moldm^{-3} of SDBS + TTAB mixture in aqueous NaBr

0.001 M NaBr			0.005 M NaBr		
α_{SDBS}	cmc	cmc*	α_{SDBS}	cmc	cmc*
0.000	35.6 ± 0.19	35.6	0.000	25.5 ± 0.28	25.5
0.0363	37.0 ± 0.27	34.8	0.0300	25.6 ± 0.49	25.3
0.0736	37.2 ± 0.38	34.0	0.0618	26.0 ± 0.24	25.0
0.1120	37.3 ± 0.49	33.1	0.0954	27.4 ± 0.68	24.8
0.1514	38.2 ± 0.69	32.4	0.1299	28.0 ± 0.63	24.5
0.1925	39.7 ± 0.88	31.6	0.1661	29.9 ± 2.6	24.2
0.3002	39.0 ± 1.4	29.7	0.2639	35.5 ± 2.1	23.5
0.4177	35.7 ± 3.1	27.9	0.3740	33.6 ± 3.7	22.8
0.8020	31.4 ± 2.2	23.2	0.7720	26.8 ± 3.9	20.5
0.8655	27.2 ± 2.2	22.6	0.8432	23.9 ± 3.8	20.1
0.9314	25.2 ± 1.2	22.0	0.9190	22.3 ± 2.4	19.8
1.000	21.4 ± 1.0	21.4	1.000	19.4 ± 3.2	19.4

subsequently with the decrease in the mole fraction from 1 to 0 and is the least in the case of pure SDBS. This sequence also indicates that there is a significant increase in the degree of counterion dissociation from $\alpha_{TTAB} = 1$ to 0. Strong ion pairing is also expected between the oppositely charged counterions of TTAB and SDBS, which would reduce the degree of counterion association at the micelle–solution interface. The latter effect may be facilitated by the screening of polar head group repulsions owing to the presence of opposite polarities at the respective head groups of the TTA^+ and DBS^- surfactant ions. This kind of behavior is responsible for a considerable broad inflection point in the κ curve and is expected to introduce large uncertainties in determining the cmc values, especially in the SDBS-rich region of the mixture; therefore, the cmc values at some selected mole fractions in this region were determined from air–water interfacial measurements (Fig. 2), which are free from this anomaly.

Since the variation in the conductivity of a surfactant electrolyte is quite linear before and after the break, a comparison among the mobilities of the monomeric and the micellar species over the whole mixing range can be made by computing the premicellar (S_1) and postmicellar (S_2) slopes. Both the S_1 and the S_2 values were determined from the linear regression analysis of the conductivity data in the premicellar and in the postmicellar regions with a correlation factor always much better than 0.999. Since the equivalent conductivity of a surfactant electrolyte can be written as $\Lambda = 1{,}000\kappa/C$, it is possible to approximately equate a Λ value with $1{,}000S_1$ for a highly dilute electrolyte solution [14] as in the case of the present surfactant binary mixtures. On the other hand, since the conductivity of the monomers can be assumed constant after the cmc and it would be permissible particularly for micelles of large aggregation numbers, the micellar state conductivity with reference to the monomer can be equated with the slope of the κ versus C profile in the postmicellar region. However, it is to be noted that the real ionic equivalent conductivity of the aggregated micelles can be computed if the aggregation number of the micelle is known. Similar quantities for single- and mixed-surfactant systems have already been discussed by some authors [14, 15, 16, 17, 18].

The variation of the S_1 and S_2 values of the SDBS plus HTAB and SDBS plus TTAB mixtures is depicted in Fig. 3 and indicates that with the increase in α_{SDBS}, the S_1 value remains more or less the same till $\alpha_{SDBS} \approx 0.35$ and thereafter it increases linearly. A similar but opposite variation can be observed for S_2. Also,

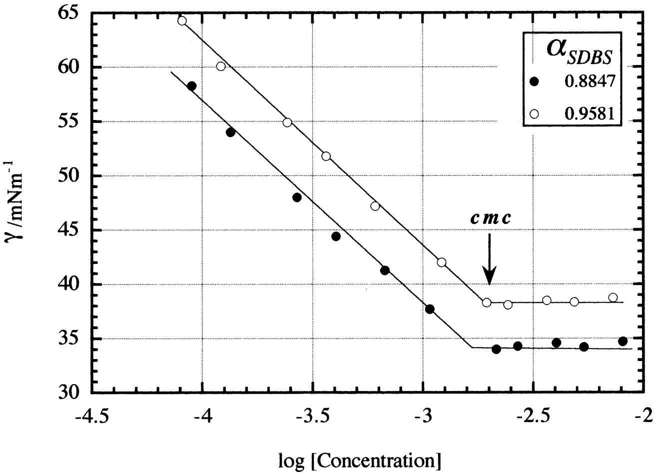

Fig. 2. Surface tension, γ, versus concentration, c, of the SDBS plus hexadecylpyridinium chloride (*HPyCl*) mixture at some selected mole fractions in pure water

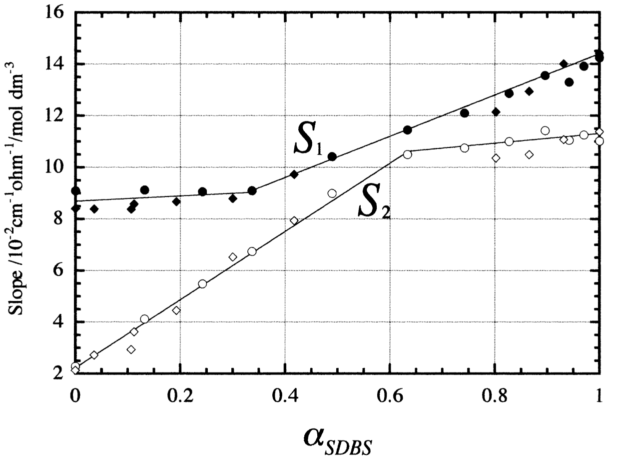

Fig. 3. Slopes versus α_{SDBS} of the SDBS plus hexadecyltrimethylammonium bromide (*HTAB*) (*circles*) and SDBS plus TTAB (*diamonds*) mixtures in pure water

similar results were observed for the SDBS plus TTPB and SDBS plus HPyCl mixtures (not shown). The initial constant value of S_1 suggests that the addition of SDBS does not have any significant influence on the monomeric conductivity till $\alpha_{SDBS}\approx0.35$; in contrast, the S_2 values show a linear increase with the increase in α_{SDBS}. Both variations can be envisaged on the basis of a higher degree of counterion dissociation in comparison to HTAB or TTAB. In the SDBS-rich region of the mixtures, a steep increase in the S_1 value and a constant S_2 value indicate the predominance of SDBS effects in the SDBS-rich region of the mixtures. Interestingly, the behavior of binary surfactant combinations consisting of SDS instead of SDBS is entirely different from that of SDBS binary mixtures. The variation in S_1 and S_2 of the SDS plus HPyCl and SDS plus TTPB mixtures is shown in Fig. 4. The S_1 values initially show a significant decrease in the case of SDS plus HPyCl and a rapid increase with the increased mole fraction of TTPB in the case of SDS plus TTPB (Fig. 4a). The former case can easily be understood on the basis of ion pairing as described in the previous cases. In contrast, surprisingly the drastic increase in the S_1 values in the case of the SDS plus TTPB mixtures in the region extremely rich in SDS, i.e., $\alpha_{SDS}\approx0.9$–1.0 is explained with the help of counterion binding in the next section. The variation in the S_2 values for the SDS plus HPyCl and SDS plus TTPB mixtures (Fig. 4b) demonstrates a positive deviation from ideality, which is most probably due to the release of counterions in the course of mixed-micelle formation.

The ratio of the S_2/S_1 values gives the degree of counterion dissociation, d, or the degree of counterion association, $\delta=1–d$. The δ values thus evaluated are usually less than those evaluated by other methods [17]; however, for the present pure surfactants they are in good agreement with those evaluated by other methods. For instance, the present δ values of SDS, HTAB, TTAB, and HPyCl are 0.45, 0.25, 0.25, and 0.42, which are in good-to-excellent agreement with 0.42 [19], 0.30 [20], 0.27 [20], and 0.42 [20], respectively. The overall variation in δ for each case of the SDBS plus cosurfactant (CS) systems is somewhat similar in all the cases (Fig. 5a). There is a large nonlinear decrease in the δ value with the increase in the amount of SDBS. It suggests that the mixed micelles become increasingly dissociated owing to a significant reduction in the polar head group repulsions as a consequence of swelling of the micelles owing to the solubilization of dimeric species up to $\alpha_{SDBS}\approx0.65$. Beyond this, δ increases slightly in the SDBS-rich region of the mixture since SDBS micelles are more ionized in comparison to the micelles of all the other CSs. Similar behavior can also be observed for the SDS plus CS systems (Fig. 5b), and the effect is very much weaker in the case of SDS plus TTPB in comparison to SDS plus HPyCl. This suggests that the higher S_1 value for the SDS plus TTPB mixture (Fig. 4a), especially in the SDS-rich region of the mixture, is probably related to the extremely small decrease

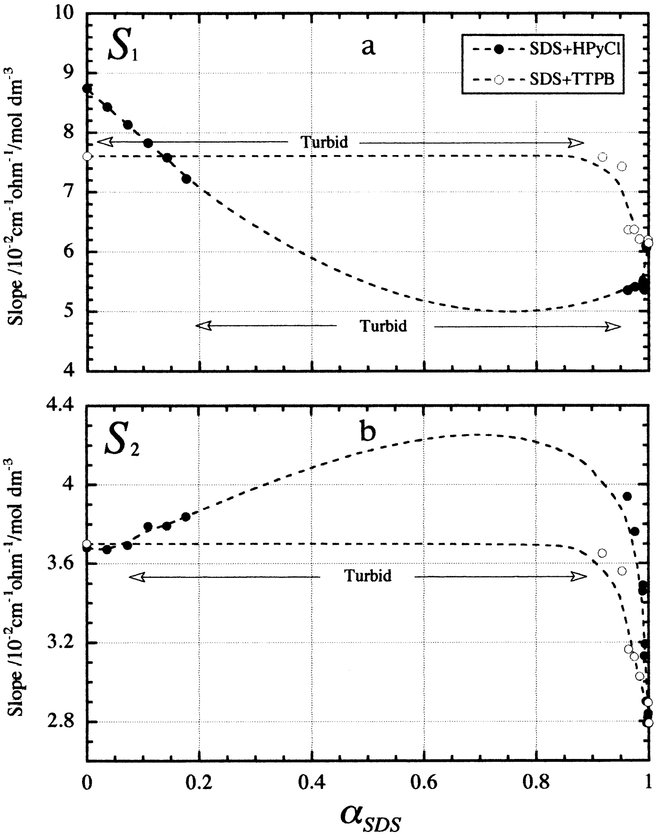

Fig. 4a,b. Slopes versus α_{SDS} of the sodium dodecyl sulfate (*SDS*) plus HPyCl and SDS plus tetradecyltriphenylphosphonium bromide (*TTPB*) mixtures in pure water

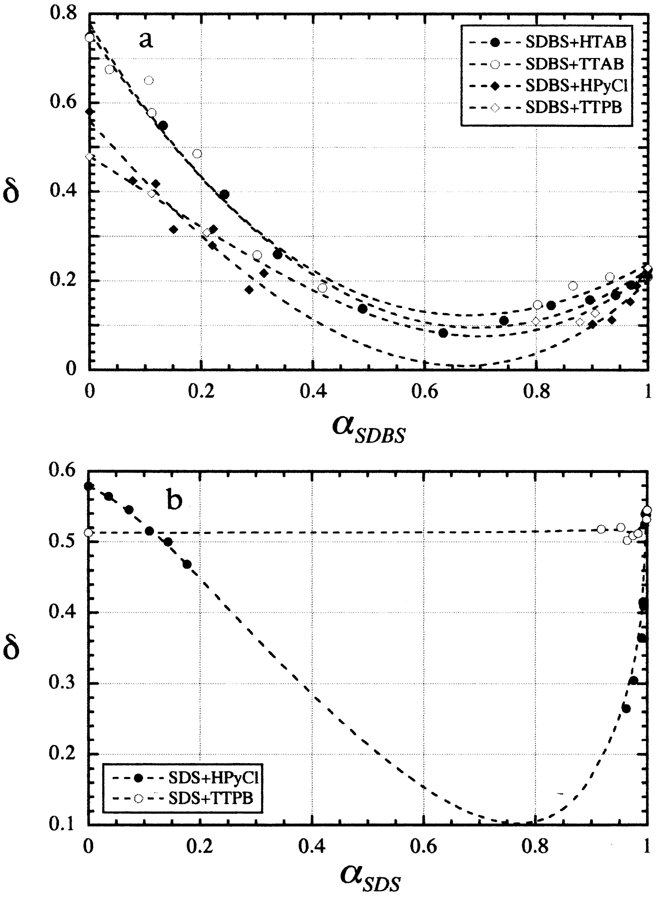

Fig. 5a,b. Degree of counterion association, δ, versus α_{SDBS} or α_{SDS} of various surfactant mixtures in pure water

in δ upon addition of TTPB in pure SDS. This could also be an indication suggesting the presence of ideality in this mixing range.

Micelle formation

The conductivity measurements also demonstrated that the sharp breaks which were quite visible in the case of pure components, for example, in the case of the SDS plus TTPB and SDS plus HPyCl mixtures (not shown), become increasingly blurred with an increase in the amount of the second component. This suggests that the micelle formation is no longer restricted to a narrow concentration range but now occurs over an appreciably wide concentration range. There are some examples [7, 21] of similar binary ionic surfactant combinations in which the breakpoint in the conductivity curve is not sharp. This can be generally explained on the basis of two situations: first, when instead of an instantaneous micelle formation process, stepwise micellization occurs as in the case of all bile salts [22] and in the presence of organic additives [23]; second, when apart from the ordinary spherical micelles, bilayer assembly [14] or insoluble salt formation take place, for example, as in the case of binary combinations of oppositely charged ionic surfactants.

The mixed cmc values listed in Tables 1, 2, 3, and 4 show conventional nonlinear behavior over the present mixing range. In order to explore the nature of the mixed micelles, i.e., whether the mixed micelles show deviations from ideal behavior, it is possible to obtain quantitative information about the formation of the micellar aggregates by using the pseudo phase thermodynamic model [24, 25]. The model relates the ideal mixed cmc (cmc*) with the experimental cmc of the pure components by using the following equations in the case of ideal mixing:

$$c_1 = x_1 \mathrm{cmc}_1 = \alpha_1 \mathrm{cmc}^* \tag{1}$$

and

$$c_2 = (1 - x_1)\mathrm{cmc}_2 = (1 - \alpha_1)\mathrm{cmc}*. \tag{2}$$

Equation (3) can be obtained after combining Eqs. (1) and (2):

$$\frac{1}{\mathrm{cmc}*} = \frac{\alpha}{\mathrm{cmc}_1} + \frac{(1 - \alpha_1)}{\mathrm{cmc}_2}, \tag{3}$$

where α_1 and x_1 are the mole fractions of surfactant 1 (SDBS or SDS) in the total mixed solute and in the mixed micelle, cmc_1 and cmc_2 and c_1 and c_2 are the cmcs and the overall concentrations involved in the micelle formation of components 1 and 2, respectively. The cmc* values thus calculated using Eq. (3) are also listed in Tables 1, 2, 3, and 4. Before discussing the nature of the mixed-micelle formation in the SDBS plus CS and SDS plus CS mixtures, some comments are necessary on the mixed-micelle formation in the SDBS plus HTAB and SDBS plus TTAB mixtures in view of their opposite behavior (Fig. 6a). The experimental cmc values for SDBS plus HTAB are lower and for the SDBS plus TTAB mixtures higher than the cmc* values evaluated from the Clint equation (Eq. 3). In both the mixtures considerably strong interactions are expected and these are responsible for the mixed-micelle formation. The significant cloudiness in the case of SDBS plus TTAB can be attributed to the formation of insoluble dimers owing to the neutralization of oppositely charged surfactant ions over a wide concentration range in comparison to SDBS plus HTAB. The larger cmc than cmc* values are generally explained on the basis of unfavorable interactions [26], and there are no grounds in the case of oppositely charged surfactants on which we could explain the unfavorable interactions. In the case of the SDS plus HPyCl mixtures (Fig. 6b), the nonideal behavior is quite different from rest of the mixtures. In the HPyCl-rich region of the mixture, i.e., $\alpha_{SDS} \approx 0.0$–0.2,

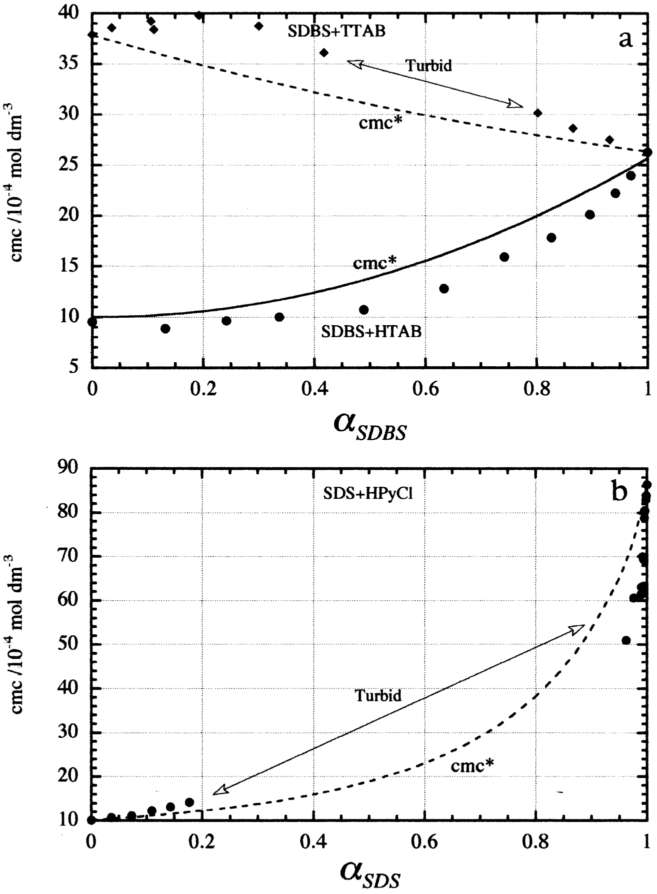

Fig. 6a,b. Critical micelle concentration (*cmc*) versus α_{SDBS} or α_{SDS} of various surfactant mixtures in pure water. Experimental cmc (*symbols*); predicted cmc* (*solid line*)

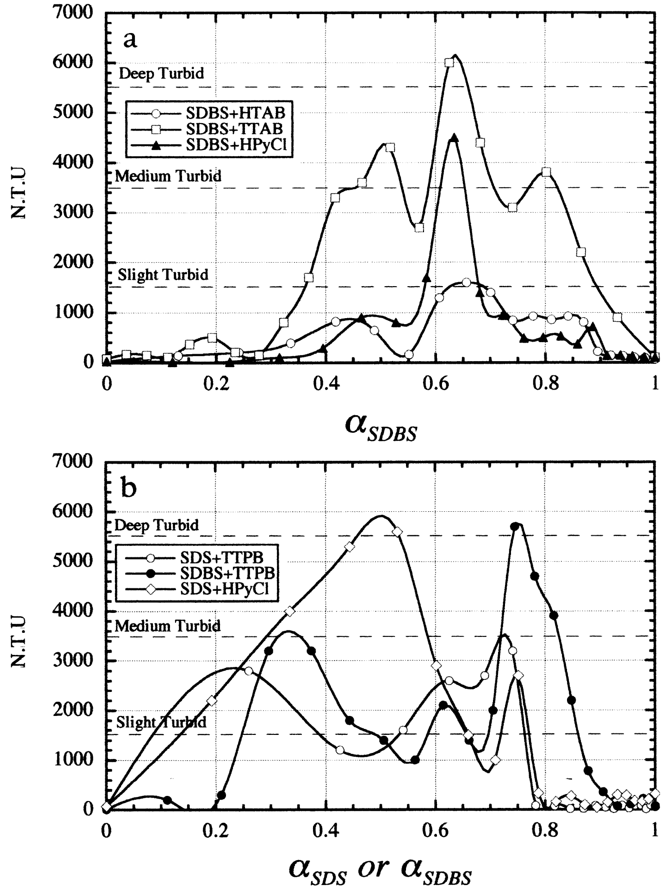

Fig. 7a,b. Turbidity versus α_{SDBS} or α_{SDS} of various surfactant mixtures in pure water

the experimental cmcs show positive deviations from the ideal cmc*, whereas in the SDS-rich region, i.e., $\alpha_{SDS}\approx 0.95$–1.0, they have negative deviations. Similar behavior has already been reported by Haque et al. [27]. These unusual results have been further explained on the basis of turbidity measurements (Fig. 7).

A comparison of the SDBS plus HTAB and SDBS plus TTAB plots shows that the SDBS plus TTAB mixture is significantly turbid over most of the mole fraction range, whereas slight turbidity was observed at a few mole fractions in the case of the SDBS plus HTAB mixtures (Fig. 7). Since the appearance of turbidity is a consequence of the formation of insoluble dimers owing to the strong electrostatic interactions, these electrostatic interactions between the oppositely charged surfactant ions are stronger in the case of SDBS plus TTAB rather than in the case of SDBS plus HTAB. One would certainly expect stronger interactions in the former case on the basis of the smaller ionic size of TTA$^+$ than HTA$^+$. However, the positive deviation of the cmc of SDBS plus TTAB from cmc* does not support this fact, which means that dimer formation between DBS$^-$ and TTA$^+$ ions takes place in the premicellar region (Fig. 3) with the result that fewer monomers would be available for the mixed-micelle formation process. Thus, the cmc is reached later and becomes greater than cmc* (Fig. 6). However, in the case of the SDBS plus HTAB mixture, the stronger hydrophobic interactions in the mixed micelles are very capable of solubilizing dimers formed in the premicellar region, consequently leading to the appearance of low turbidity. One can also observe a similar situation in the case of the SDS plus HPyCl mixture, where considerable turbidity appears in the HPyCl-rich region of the mixture, and the SDS region, i.e., $\alpha_{SDS}\approx 0.8$–1.0, remains quite clear (Fig. 7b). Again, the HPyCl-rich region shows a positive deviation of the cmc from the cmc* value in this region (Fig. 6b). Hence, it seems that there is a strong correlation between the turbidity and the positive nonideality of strongly interacting surfactants owing to which the mixed cmc increases more than its intended value due to the unavailability of surfactant monomers.

Since the mixing behavior of the oppositely charged surfactant mixtures shows strong deviations from ideal behavior, these results were further evaluated by using the regular solution formulation [25], which relates the mixed cmc to the individual cmc, i.e,. cmc_1 and cmc_2, by

$$c_1 = x_1\mathrm{cmc}_1 f_1 = \alpha_1\mathrm{cmc} \tag{4}$$

and

$$c_2 = (1 - x_1)\mathrm{cmc}_2 f_2 = (1 - \alpha_1)\mathrm{cmc}, \tag{5}$$

where f_1 and f_2 are the activity coefficients of surfactant 1 (SDBS or SDS) and surfactant 2 (CS) respectively. x_1 can be computed from the following equation:

$$\frac{x_1^2 \ln(\mathrm{cmc}\alpha_1/\mathrm{cmc}_1 x_1)}{(1 - x_1)^2 \ln[\mathrm{cmc}(1 - \alpha_1)/\mathrm{cmc}_2(1 - x_1)]} = 1. \tag{6}$$

Equation (6) can be solved iteratively to obtain the value of x_1. From x_1, the interaction parameter, β, can be computed by using the following equation:

$$\beta = \frac{\ln\left(\frac{\mathrm{cmc}\alpha_1}{\mathrm{cmc}_1 x_1}\right)}{(1 - x_1)^2}. \tag{7}$$

The β value demonstrates the extent of the interactions between the two surfactants which lead to the deviations from the ideal behavior. In the literature, large negative β values have been reported for oppositely charged ionic surfactant combinations [2, 4]. The β values evaluated for the present binary mixtures are shown graphically in Fig. 8a. It is interesting to observe that all the SDBS plus TTAB mixtures, i.e., in pure water as well as in the presence of aqueous NaBr, show a strong dependence of β on α_{SDBS} and have large positive β values especially in the SDBS-rich region of the mixtures. It is to be noted that significant cloudiness was observed particularly in this region of the mixture (Fig. 7a). In contrast, the β values for the SDBS plus HTAB and SDBS plus TTPB mixtures show mainly constant variation and average β values of –0.94 and –0.33, respectively. Large negative β values showing a dependence on α_{SDS} were obtained in the case of the SDS plus TTPB and SDS plus HPyCl mixtures (Fig. 8a). Furthermore, a variation in the micellar mole fraction (x_1) (Fig. 8b) suggests that the x_1 values in the case of the SDBS plus TTAB mixtures in the TTAB- and SDBS-rich regions are lower and slightly higher than the ideal behavior, respectively. This suggests that mixed micelles are rich in SDBS in the TTAB-rich region and vice versa. On the other hand, the x_1 values for all the other mixtures indicate that the mixed micelles of these mixtures are mainly occupied by the monomers of CSs. Collectively, it can be said that in the case of all the present binary mixtures wherever there was no or slight cloudiness (Fig. 7), the mixed micelles show synergistic interactions and they are rich in the CS component which is always more hydrophobic than either SDBS or SDS.

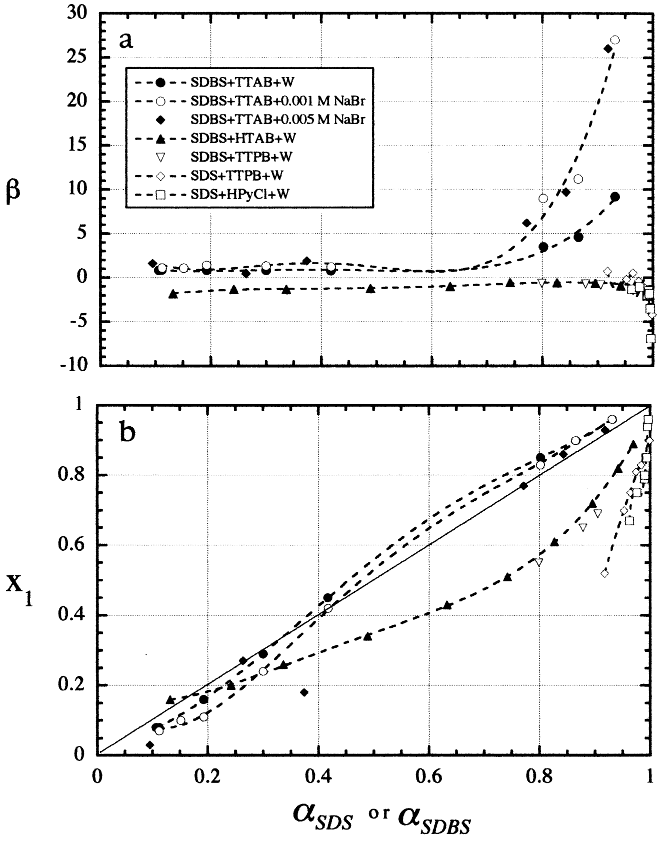

Fig. 8. **a** β versus α_{SDBS} or α_{SDS} of various surfactant mixtures in pure water. **b** x_1 versus α_{SDBS} or α_{SDS} of various surfactant mixtures in pure water

Viscometric behavior

In order to further explore the influence of the nature of the head group on the mixed-micelle formation, we carried out viscometric studies, which are quite sensitive to the ongoing structural changes in the spherical micelles under the effect of head-group variation. Apart from this, the viscometric studies are also expected to throw light on the presence of synergism in the present mixtures. We measured the relative viscosities, η_r, of all the binary mixtures at the same concentrations and mole fractions as were used for the conductivity measurements. The variation in the η_r values for the SDBS plus HTAB and SDBS plus TTAB mixtures in pure water as well as in the presence of aqueous NaBr is shown in Fig. 9a. It can be seen η_r decreases as soon as there is an increase in the amount of SDBS in pure HTAB or TTAB micelles up to $\alpha_{\mathrm{SDBS}}\approx 0.3$, and thereafter it increases exponentially with a further increase in the amount of SDBS. The initial decrease in η_r can be attributed to the formation of compact mixed micelles, which is obviously due to some favorable interactions, and the mixture remains clear up to $\alpha_{\mathrm{SDBS}}\approx 0.3$ (Fig. 7a, turbidity

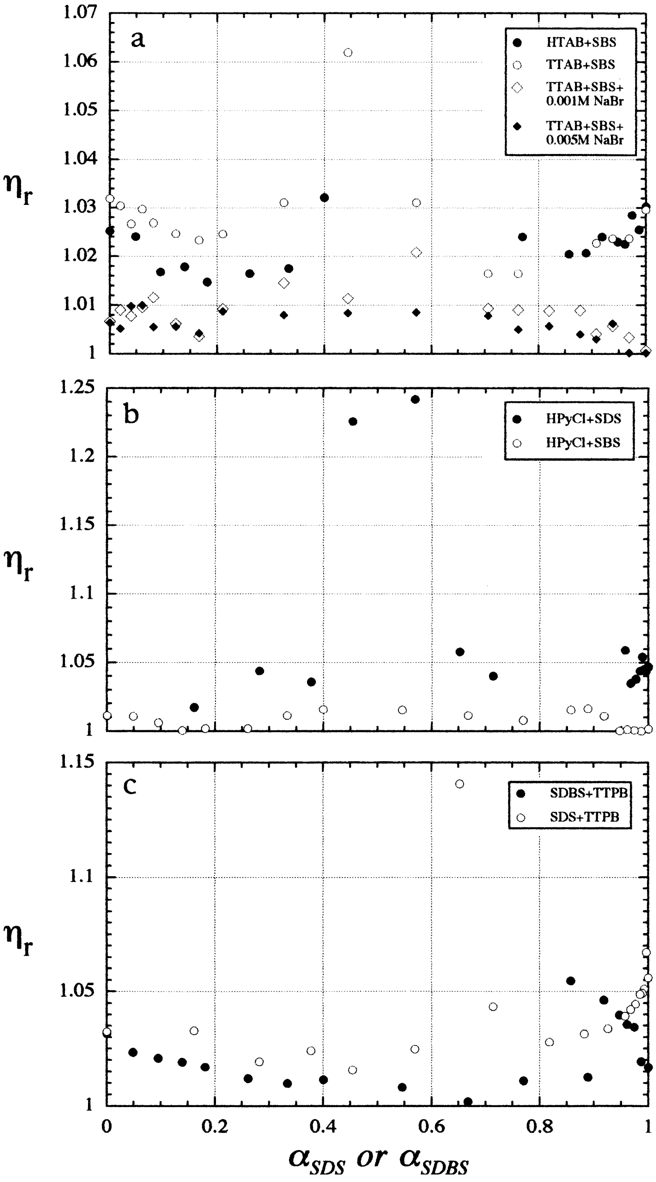

Fig. 9a–c. η_r versus α_{SDBS} or α_{SDS} of various surfactant mixtures in pure water and in aqueous NaBr

measurements were also carried out at an equivalent concentration to that of the conductivity measurements.). Thereafter, insoluble dimer formation starts at the concentration which is demonstrated by an instantaneous increase in η_r (Fig. 9a) and by the appearance of cloudiness in the solution (Fig. 7a). Furthermore, in the SDBS-rich region of the mixture, especially within $\alpha_{SDBS}\approx0.8$–1.0, where slight turbidity appears (Fig. 7b), η_r remains almost the same for both mixtures, confirming the earlier conclusion that both mixed micelles are mainly occupied by SDBS monomers (Fig. 8b). In the presence of 0.001 and 0.005 M NaBr (Fig. 9a), η_r of the SDBS plus TTAB mixture is significantly difference from that in pure water. First of all, as expected, η_r of pure SDBS and TTAB micelles in aqueous NaBr solution is significantly less than that in pure water, indicating the formation of even more compact micelles owing to effective neutralization of polar head group repulsions caused by the adsorption of excess counterions at the micelle–solution interface. Induction of SDBS in the TTAB-rich region and vice versa produces a slight increase in the η_r value, most probably owing to the decrease in the compactness of the respective pure micelles on the basis of packing geometry [28] reasons. The latter might have arisen when unlike bulky polar head groups wanted to adjust in the restricted spherical arrangement of the mixed micelles. Thus, the presence of salt will in no way increase the stability of the mixed micelles but in fact it supports the antagonism already existing owing to the steric or packing geometry constraints and with the result that even the β value remains positive over the whole mixing range (Fig. 8a).

An interesting comparison between the viscometric behavior of the HPyCl plus SDS and HPyCl plus SDBS mixtures is also demonstrated in Fig. 6. The former mixture shows a significant increase in η_r close to equimolar proportions in comparison to the latter and the same is so in the case of the turbidity (Fig. 7). Since no cmc values were evaluated in the turbid regions of both mixtures, the respective synergism was evaluated from the data obtained mainly from the extremely rich regions of both components of these mixtures. As expected, the HPyCl plus SDS mixture shows a significant increase in the negative β value with an increase in the amount of SDS in the SDS-rich region (Fig. 8a), while a negative β value is also obtained in the case of the HPyCl plus SDBS mixture. The latter is significantly smaller and remains invariant with respect to α_{SDBS} (the average β value is –1.2). This suggests that the replacement of SDS by SDBS induces large geometrical packing problems with the result that the extent of synergism reduces significantly. A similar situation exists in the case of the TTPB plus SDS and TTPB plus SDBS mixtures (Fig. 9c).

Furthermore, if we compare the mixed-micelle formation between SDBS plus TTAB and SDS plus HPyCl, one thing is quite common in both cases – they show medium to significant cloudiness over most of the mixing range (Fig. 7a, b, respectively); however, close inspection of the plots of both mixtures indicates that the TTAB-rich region in the former case ($\alpha_{SDBS}\approx0.0$–0.2) and the SDS-rich region in the latter case ($\alpha_{SDBS}\approx0.8$–1.0) are almost free from cloudiness. This means that cloudiness occurred in the SDBS- or HPyCl-rich regions of the mixtures owing to the dimer formation; it vanishes upon addition of the second component. Again one thing is common between SDBS and HPyCl – the head groups of both surfactants possess aromatic character and this is not the case with either TTAB or SDS; therefore, the addition of a surfactant possessing a nonaromatic head group in a micelle of a surfactant with an aromatic head group induces the cloudiness which can also be observed in the case of the SDS plus TTPB mixture (Fig. 7b). In the latter case, TTPB is weak at solubilization of TTPB–SDS dimers in comparison to SDS. Interestingly, when both components possess aromaticity, as in the case of the SDBS plus TTPB mixture, the cloudiness is observed almost over most of the mole fraction range. This means that the surfactant with an aromatic head group remains weak to solubilize sparingly soluble dimers; hence, the cloudiness persists in the rich region of surfactant with an aromatic head group.

These results suggest the appearance of cloudiness is mainly related to the packing geometry, especially in those oppositely charged surfactants which possess monomers with unlike bulky polar head groups as in the case of the SDBS plus TTAB, SDBS plus TTPB, SDS plus TTPB, and SDS plus HPyCl mixtures. Thus, the packing geometry problems arise in the micelles, which are made up solely of monomers of aromatic character with bulky polar head groups upon addition of oppositely charged monomers with nonaromatic head groups. This is due to the fact that the micelles of the former are already loose micelles, and these are expected to be quite sensitive to packing problems especially in the case of the SDBS plus TTAB, SDS plus HPyCl, and SDS plus TTPB mixtures. On the other hand, this is not the case with the micelles of monomers with nonaromatic head groups, which are comparatively more compact than the former ones. Hence, they are relatively more stable and can accommodate initially oppositely charged monomers with aromatic head groups without any significant packing problems in the head-group region, for example, in the case of the CS-rich region of all the the mixtures in Fig. 7a and the SDS-rich region of the mixtures in Fig. 7b. Therefore, the instability in the loose mixed micelles for packing reasons in the head-group region leads to the destruction of mixed micelles in the form of insoluble salts, whereas this is prevented by the stable mixed micelles in the latter case and hence no cloudiness appears.

Conclusions

The mixed-micelle formation between strongly interacting surfactants with bulky head groups was studied. It was found that head-group modification significantly influences the nature of mixed-micelle formation. Although there are only two methylene groups more in HTAB than in TTAB, the binary mixtures of TTAB plus SDBS show significant cloudiness over most of the mole fraction range, whereas this is not so in the case of HTAB plus SDBS, with the result that the experimental mixed cmc of the former even exceeds the ideal cmc (cmc*) evaluated from the Clint equation. This lead to the evaluation of the positive β value, which even remains more or less the same in the presence of aqueous NaBr. A similar situation also exists especially in the HPyCl-rich region of the SDS plus HPyCl mixture where again significant cloudiness appeared. On the other hand, predominantly strong negative β values were obtained especially at those mole fractions in all the cases where no turbidity was observed. These results were explained on the basis of the fact that upon becoming cloudy, the concentration of the monomers decreases in the solution more than required, with the result that the experimental mixed cmc increases and even exceeds the cmc* value.

The viscometric studies have confirmed the previously mentioned behavior in every mixture. In all the cases in pure water, stable mixed-micelle formation was demonstrated by an initial decrease in η_r, especially in the respective rich regions of the components. An instantaneous increase in η_r was observed at those mole fractions where medium to significant cloudiness appeared. The presence of NaBr was found to increase the incompatibility between the TTAB and SDBS monomers.

Acknowledgements Financial assistance from the DST under a research project (ref. no. SP/S1/H-22/2001) is thankfully acknowledged. I.K. thanks the CSIR, New Delhi, for a Junior Research Fellowship.

References

1. Motomura K, Aratono M (1993) In: Ogino K, Abe M (eds) Mixed surfactant systems. Dekker, New York, pp
2. Holland P, Rubingh D (1991) In: Holland P, Rubingh D (eds) Cationic surfactants, vol 37. Dekker, New York, chap 4
3. Moroi Y (1992) Micelles, Theoretical and applied aspects. Plenum, New York
4. Jonsson B, Lindman B, Holmberg K, Kronberg B (eds) (1998) Surfactants and polymers in aqueous solutions. Wiley, New York
5. Zhu BY, Rosen MJ (1984) J Colloid Interface Sci 99:435
6. Holland PM, Rubingh DN (1983) J Phys Chem 87:1984
7. Matsuki H, Aratono M, Kaneshina S, Motomura K (1997) J Colloid Interface Sci 191:120
8. Kaler EW, Murthy AK, Rodriguez BE, Zasadzinski JAN (1989) Science 245: 1371
9. Lange H, Schwuger MJ (1971) Kolloid Z Z Polym 243:120
10. Amante JC, Scamehorn JF, Harwell JH (1991) J Colloid Interface Sci 144:243
11. Ozeki S, Ikeda S (1980) J Colloid Interface Sci 77:219

12. Bakshi MS (1993) J. Chem Soc Faraday Trans 89:4323
13. Bakshi MS (1997) J Chem Soc Faraday Trans 93:4005
14. Treiner C, Makayssi A (1992) Langmuir 8:794
15. Manabe M, Kawamura H, Yamashita Y, Tokunaga S (1990) In: Bloor BM, Wyn-Jones E (eds) The structure, dynamics and equilibrium properties of colloidal systems. Kluwer, The Netherlands, pp 63–69
16. Okubo T, Kitano H, Ise N (1976) J Phys Chem 80:2661
17. Sugihara G, Hisatomi M (1998) J Jpn Oil Chem Soc 47:661
18. Sugihara G, Era Y, Funatsu M, Kunitake T, Lee S, Sasaki Y (1997) Colloid Interface Sci 187:345
19. Lin SY, Lin YY, Chen EM, Hsu CT, Kwan CC (1999) Langmuir 15:4370
20. Moulik SP, Haque ME, Jana PK, Das AK (1996) J Phys Chem 100:701
21. Sarmiento F, Lopez-Fontan JL, Prieto G, Attwood D, Mosquera V (1997) Colloid Polym Sci 275:1144
22. Haque ME, Das AK, Moulik SP (1999) J Colloid Interface Sci 217:1
23. Bakshi MS (1996) Bull Chem Soc Jpn 69:2723
24. Clint JH (1975) J Chem Soc Faraday Trans 1 71:1327
25. Rubingh DN (1979) In: Mittal KL (ed) Solution chemistry of surfactants, vol 1. Plenum, New York, p 337
26. Somasundaran P, Huang L (1999) In: Lange KR (ed) Surfactants. Hanser, Munich, p 204
27. Haque ME, Das AR, Rakshit AR, Moulik SP (1996) Langmuir 12:4084
28. Hayter JB, Penfold J (1983) J Colloid Polym Sci 261:1022
29. Mateos IG, Velazquez MM, Rodriguez L (1990) Langmuir 6:1078
30. Lopez-Fontan JL, Suarez MJ, Mosquera V, Sarmiento F (2000) J Colloid Interface Sci 223:185