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ORIGINAL CONTRIBUTION

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The interaction of isomeric hexanediols with sodium dodecyl sulfate and dodecyltrimethylammonium bromide micelles

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Abstract The micelle formation process for a typical anionic surfactant, sodium dodecyl sulfate, and a typical cationic surfactant, dodecyltrimethylammonium bromide, has been investigated in a series of mixed solvents consisting of different concentrations of isomeric hexanediols (1,2-hexanediol and 1,6-hexanediol) in water. The critical micelle concentrations and the degrees of counterion dissociation of the mixed micelles were obtained from conductance experiments. Luminescence probing experiments have been used to determine the concentration of micelles in solution and, hence, the micellar aggregation numbers of the surfactants in the mixed solvent systems. The alcohol aggregation numbers were determined by combining the partition coefficients (obtained using NMR paramagnetic relaxation enhancement experiments) with the micellar concentrations from the luminescence probing experiments. All these results are interpreted in terms of the difference in the interaction of the isomeric hexanediols with the surfactant as a function of the position of the hydroxyl groups on the six-carbon chain of the alcohol.

Key words Mixed micelles · Surfactants · Aggregation numbers · Critical micelle concentration

Introduction

A number of industrially important properties of surfactants are enhanced with the addition of a second surface-active molecule (a cosurfactant). Alcohols and amines are common cosurfactants for many applications. A wide variety of fundamental investigations into the properties of alcohol/surfactant mixed micellar systems have been carried out mainly owing to the importance of these aggregated systems in various applications [1–30]. Most of these studies have focussed on the influence of cosurfactant (i.e., the alcohol or amine) on a single property of the host micelles as a function of the additive concentration (e.g., critical micelle concentrations, cmc, aggregation numbers of the surfactant, or degrees of counterion dissociation, α. However, a key parameter in understanding the fundamental properties of mixed micelle systems is to determine the degree to which additives penetrate the micellar phase. The mole fraction of solubilizates (additives) in the micellar phase, p, is defined as

$$p = \frac{c_{\mathrm{a,mic}}}{c_{\mathrm{a,t}}} \quad , \tag{1}$$

where $c_{\mathrm{a,mic}}$ is the concentration of solubilizate in the micellar phase and $c_{\mathrm{a,t}}$ represents the total concentration of additive [30]. The degree of solubilization of alcohols in mixed micelles has been obtained using many different methods. Hayase and Hayano [9] used vapour-pressure measurements by gas chromatography to determine the partition coefficients of various primary alcohols. Likewise, Spink and Colgan [10] used vapour-pressure measurements to determine the fraction of 1-heptanol in various anionic micelles. In addition, solubility experiments [6] and NMR measurements [24] have also been used to determine partition coefficients. The NMR paramagnetic relaxation experiment, originally proposed by Gao et al. [28] and later used by Marangoni and Kwak [27] and Gao et al. [29], has been successfully employed to determine the partition coefficients of solubilizates in a number of aggregated systems.

Despite the vast literature that has developed on the interactions of alcohols with micelles, there has been little research done on the interaction of different families of alcohols (such as alkanediols) with anionic and cationic micelles. The placement of the second headgroup should have an impact on how the diol interacts with the micelle and, hence, how it alters the properties of the mixed aggregates. However, previous work done with isomeric butanediols [30] indicated that the placement of the hydroxyl groups on the carbon backbone made little difference with respect to the critical micelle concentrations (cmc) and the thermodynamic properties of micelle formation, which is likely to be the result of the small hydrocarbon chain on the alcohol. For monohydroxy alcohols, it has previously been reported that 3- and 4-heptanols are solubilized mainly at the surface of the micelle, while 1- and 2-heptanols are more likely to be solubilized in the interior of the micelle rather than on the surface [26]. The difference in the degree of solubilization must, therefore, be related to the position of the hydroxyl group on the hydrocarbon chain. The hydroxyl group will maintain favourable hydrogen bonding with the water molecules located near the micellar surface, while the alcohol hydrocarbon chain will interact with the hydrocarbon chain of the surfactant in the micellar interior. When located in the middle of a medium-sized hydrocarbon chain, as in the case of 3-heptanol, only the ends of the molecule are free to mix with the interior of the micelle, whereas for 1-heptanol, the hydroxyl group is on the end of the chain, resulting in greater penetration of the alcohol chain into the micellar interior and, hence, increased alkyl chain interactions.

The purpose of the present work was to investigate the effect of the longer-chain diols on the fundamental properties of micelle formation. The cmcs of the mixed micelle system as a function of alcohol concentration were obtained from conductance measurements. The partition constants, p, from the NMR–paramagnetic relaxation experiment (PRE) experiments were used to estimate the Gibbs energy of transfer of the alcohol, $\Delta_{\mathrm{tr}}G^0$, from the aqueous phase to the micellar phase. The aggregation numbers of the surfactant and the alcohol molecules, also as a function of the alcohol concentration, were determined from luminescence probing experiments and NMR–PRE experiments. All these results were interpreted in terms of the effect of the placement of the second hydroxyl group on the carbon backbone on the properties of the surfactant/hexanediol (HXD) mixed micelles.

Experimental

Materials

Sodium dodecyl sulfate (SDS) was obtained form OmniPur at 99% purity. The dodecyltrimethylammonium bromide (DTAB) was obtained from Sigma and was purified by repeated recrystallizations in an acetone/ethanol mixture. Triply deionized water of conductance grade was obtained from a Millipore ion-exchange system. 1,6-HXD was obtained from Aldrich at 97% purity. The 1,2-HXD was obtained from Fluka also at 97% purity. The fluorescence probe, pyrene, was obtained from Aldrich and was purified by sublimation. The quencher, cetylpyridium chloride monohydrate (CPC), was also obtained from Aldrich and it was purified by repeated recrystallization from an acetone/ethanol mixture.

Methods and solution preparation

cmc determinations

Solutions of the anionic and cationic surfactants in the various mixed solvent systems were prepared in volumetric flasks using the appropriate amount of surfactant and alcohol in deionized water. All surfactant and alcohol concentrations are expressed in molarity units, where the molarity is defined as the number of moles of surfactant per litre of the mixed solvent. The cmc values for the surfactant/HXD systems were obtained from the break-in plots of the conductance titrations; these are reported in terms of the number of moles of surfactant per litre of the mixed solvent system. The conductance values of the solutions were measured as a function of the concentration of surfactant using a YSI conductance bridge with a conductance cell with $K_{\mathrm{cell}} \sim 1\ \mathrm{cm}^{-1}$. A Brinkman 250 automatic burette was used to add increments of surfactant/HXD solutions to the mixed solvent; the temperature of the conductance cell was maintained within ±0.05 °C using a Julabo water bath.

NMR experiments [27, 28]

All of the spin-lattice relaxation times, T_1, were measured using freshly prepared solutions. A solution of the paramagnetic spin probe, the sodium salt of 3-carboxyPROXYL for anionic micelles or a solution of $MnCl_2$ in D_2O for cationic micelles, was made up in D_2O (99.9% Aldrich). SDS solutions of 70 g/l (about 243 mM) and DTAB solutions of 50 g/l (about 162 mM) were made up either directly in the NMR tube or in small glass vials with either the D_2O or the paramagnetic ion solution as the solvent. 1,2-HXD (10 μl) was added directly to the NMR tubes with a Hamilton syringe, whereas 10 mg 1,6-HXD was added directly to the SDS or DTAB solution in the NMR tubes or in the glass sample vials. The measurements of T_1 were carried out at 24 ± 1 °C and were obtained using the standard inversion-recovery pulse program in the Braker software library. These values were calculated from the peak heights obtained from at least 12 variable delays, using a three-parameter, nonlinear least-squares fitting procedure. The errors in T_1 are estimated from the reproducibility of T_1 in separate trials.

Luminescence probing experiments

All the solutions for the luminescence probing experiments were made up on a molar basis. A small amount of a pyrene/ethanol solution was placed in the bottom of a beaker; the ethanol was allowed to evaporate, leaving a thin film of pyrene deposited over the bottom of the flask. The surfactant/HXD solution of the desired concentration was placed in the beaker and the solution was stirred vigorously for a minimum of 4–5 h (and usually overnight) to ensure complete dissolution of the pyrene into the surfactant micelles. Half of the solution was then used to make a 1–2 mM CPC (the quencher) solution. This quencher solution was stirred for 1–2 h to ensure that the CPC was dissolved in the micelles. Solutions with varying amounts of quencher were prepared so that the amount of quencher was between 0 and 1–2 mM. Steady-state pyrene fluorescence emission spectra were recorded using an Aminco-Bowman 2300 spectrophotometer. The heights of the first (I_1) and third (I_3) emission peaks were recorded directly from the spectra. The intensities of the first emission peak were used in the plot of $\ln(I_0/I)$ versus quencher concentration to determine the aggregation numbers for the mixed micellar systems.

Results and discussion

cmc and α values for surfactant/alcohol mixed micelles

The cmc values for the SDS/HXD mixed micelles, obtained from the breaks in the conductance versus $c_{\mathrm{surf,t}}$ plots, are presented in Table 1 and are plotted in Fig. 1 as a function as the total concentration of alcohol. The cmc values for the DTAB/HXD mixed micelles are also presented in Table 1 and are plotted in Fig. 2 as a function of the total concentration of alcohol. When we examine the cmc values for the surfactant/HXD systems (Figs. 1, 2, respectively), we observe the expected initial, linear decrease in the cmc of the surfactant as the amount of alcohol in the solvent is increased. Also, we can clearly see from the two figures that the addition of the 1,2-HXD to the mixed solvent initially decreases the cmc to a much greater extent than the 1,6-HXD at the same alcohol concentration. This reduction in the cmc with increasing alcohol concentration is a combination of the decrease in the electrostatic repulsions in the headgroup region (due to the presence of two nonionic headgroups in the alcohol) and the increase in the van der Waals interactions as the hydrocarbon chains of both the surfactant and the alcohol mix in the micellar interior. Hence, the Gibbs energy of the system is lowered, which would in turn lead to a lower cmc value. For the SDS/1,2-HXD systems versus the SDS/1,6-HXD systems, the decrease in the mixed cmc values at the same alcohol concentration may be due to the fact that the two adjacent headgroups for the 1,2-HXD have a larger effect on the electrostatic part of $\Delta_{\mathrm{mic}}G^0$ and, hence, may be more effective in lowering the cmc of the mixed micelles; however, it may also be due to an increase in the alcohol partition coefficient of the 1,2-HXD over that of the 1,6-HXD (see later). With an increase in the partition constant, a larger quantity of alcohol is present in the micellar phase as the amount of

Table 1 cmc values (±0.5 mM) for sodium dodecyl sulfate (*SDS*)/hexanediol (*HXD*) and dodecyltrimethylammonium bromide (*DTAB*)/HXD mixed micelles as a function of the concentration of alcohol added

c_a/M	SDS/ 1,2-HXD	SDS/ 1,6-HXD	c_a/M	DTAB/ 1,2-HXD	DTAB/ 1,6-HXD
0.000	8.3	8.3	0.000	15.0	15.0
0.025	7.2	7.7	0.025	14.4	14.9
0.050	6.2	7.5	0.050	13.6	14.8
0.075	5.4	7.2	0.075	12.8	14.5
0.100	4.8	6.7	0.100	12.4	14.2
0.150	5.2	7.2	0.150	11.0	14.0
0.200	6.7	7.0	0.200	10.1	13.6
0.250	6.9	7.2	–	–	–

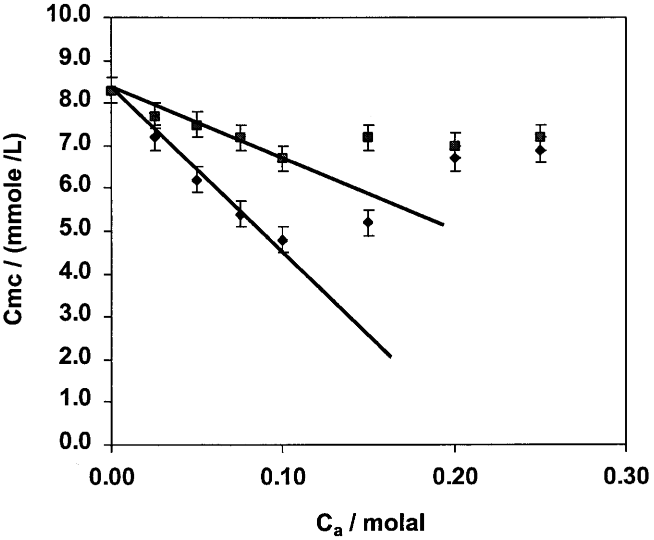

Fig. 1 cmc values for sodium dodecyl sulfate (*SDS*)/hexanediol (*HXD*) mixed micelles as a function of the molarity of the alcohol in the mixed solvent

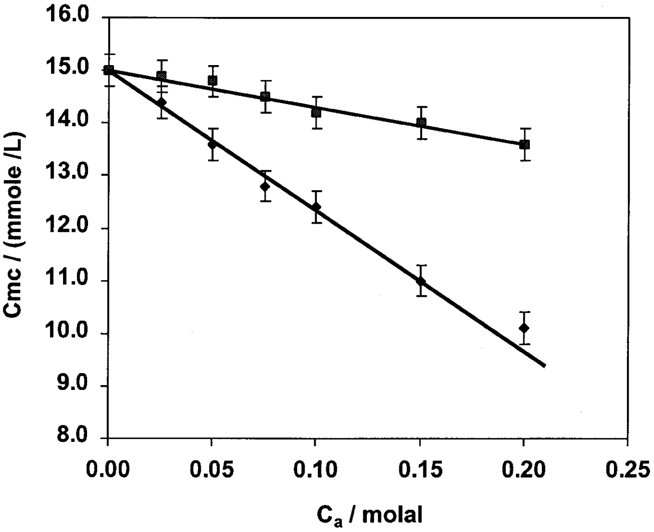

Fig. 2 cmc values for dodecyltrimethylammonium bromide (*DTAB*)/HXD mixed micelles as a function of the molarity of the alcohol in the mixed solvent

the alcohol in the mixed solvent is increased. As the micellar concentration of alcohol increases, substantial changes in both the hydrophobic and the electrostatic part of $\Delta_{\mathrm{mic}}G^0$ are expected.

The degree of counterion dissociation, α, was calculated from the conductance plots for all the surfactant alcohol systems using the ratio-of-slopes method. These values are presented in Table 2 for both the SDS/HXD systems and the DTAB/HXD systems and are plotted in Figs. 3 and 4, respectively. It is clear from Table 2 that an increase in the concentration of the HXDs in the mixed solvent system results in a systematic increase in the α values of the mixed micelles. This is due to the fact that as more alcohol is added to the system and as aggregation occurs the neutral diol molecules replace the charged surfactant monomers in the micelle. This causes a decrease in the overall surface charge on the micelles, thereby causing the degree of counterion dissociation to increase. Somewhat surprisingly, in both the SDS/HXD and the DTAB/HXD mixed systems, there is a small difference in the α values between the 1,2-HXD and the 1,6-HXD (the surfactant/1,2-HXD systems have slightly larger α values).

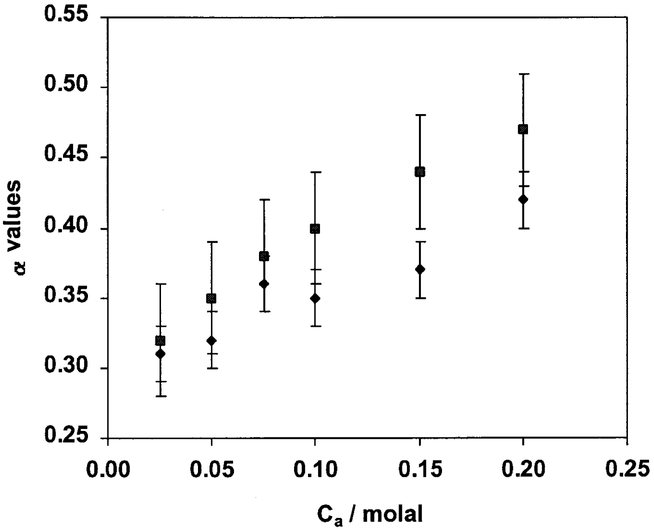

Fig. 4 Degrees of counterion dissociation (α values) for DTAB/HXD mixed micelles as a function of the molarity of the alcohol in the mixed solvent

Table 2 Degree of counterion dissociation (α values) for SDS/HXD and DTAB/HXD mixed micelles as a function of the concentration of alcohol added

c_a/M	SDS/ 1,2-HXD	SDS/ 1,6-HXD	c_a/M	DTAB/ 1,2-HXD	DTAB/ 1,6-HXD
0.000	0.39	0.39	0.000	0.31	0.31
0.025	0.44	0.42	0.025	0.32	0.31
0.050	0.49	0.46	0.050	0.35	0.32
0.075	0.53	0.50	0.075	0.38	0.36
0.100	0.56	0.53	0.100	0.40	0.35
0.150	0.64	0.60	0.150	0.44	0.37
0.200	0.67	0.64	0.200	0.47	0.42
0.250	0.66	0.67	–	–	–

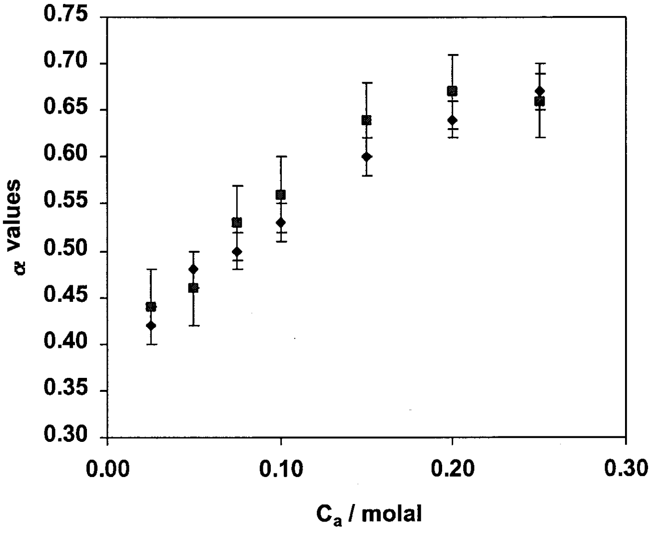

Fig. 3 Degrees of counterion dissociation (α values) for SDS/HXD mixed micelles as a function of the molarity of the alcohol in the mixed solvent

The increases in the α values of the alcohol/surfactant mixed micelles with increasing alcohol concentration are again due to a combination of electrostatic and hydrophobic effects. The size and structure of the surfactant headgroup may make an important contribution to the screening or shielding of the adjacent surfactant headgroups, whereas the increase in the partition coefficient for the more hydrophobic alcohols increases the number of cosurfactant molecules in the micelles. Both of these effects lead to changes in the surface charge density of the mixed micelle, which, in turn, affects the degree of counterion dissociation.

NMR–PRE experiments

The degree of solubilization, p, of the HXD molecules in SDS micelles can be obtained from NMR relaxation experiments using the equation [30]

$$p = 1 - \frac{R_1^{\mathrm{p}}(\mathrm{obs}) - R_1(\mathrm{obs})}{R_1^{\mathrm{p}}(\mathrm{aq}) - R_1(\mathrm{aq})} \ . \qquad (2)$$

Here, $R_1^{\mathrm{p}}(\mathrm{obs})$ and $R_1(\mathrm{obs})$ are the spin-lattice relaxation rates for the HXD molecules in micellar solution in the presence and the absence of paramagnetic ions, respectively, while $R_1^{\mathrm{p}}(\mathrm{aq})$ and $R_1(\mathrm{aq})$ are the HXD relaxation rates in aqueous solution in the presence and the absence of paramagnetic ions, respectively ($R_1 = 1/T_1$). From the value of p, we have calculated the mole-fraction-based distribution coefficient, K_x, which is defined as

$$K_x = \frac{X_{mic}}{X_{aq}} \quad , \tag{3}$$

where X_{mic}, and X_{aq} are the mole fractions of solubilizate in the micellar and aqueous phases, respectively, and are defined by

$$X_{mic} = \frac{pc_{a,t}}{pc_{a,t} + \left(c_{surf,t} - c_{surf,mon}\right)} \quad , \tag{4}$$

$$X_{aq} = \frac{(1-p)c_{a,t}}{\left[(1-p)c_{a,t} + c_{surf,mon} + c_{D_2O}\right]} \quad , \tag{5}$$

where $c_{surf,t}$ and $c_{surf,mon}$ are the total and the monomeric concentrations of surfactant, respectively, c_{D_2O} is the solvent concentration and $c_{a,t}$ is the additive concentration in molar units. Equation (7) can be approximated as

$$X_{aq} = \frac{(1-p)c_{a,t}}{c_{D_2O}} \quad . \tag{6}$$

The Gibbs energy of transfer of the alcohol from the aqueous phase to the micellar phase ($\Delta_{tr}G^0$) can be calculated from the relation [31]

$$\Delta_{tr}G^0 = -RT \ln K_x \quad . \tag{7}$$

As seen in Table 3, for both the SDS and the DTAB systems, we note that 1,2-HXD partitions into the micelle to a greater degree than 1,6-HXD. This indicates that the p values vary depending on the location of the second hydroxyl group on the hexane chain. When the hydroxyl groups are in the 1,6 position on the hexane chain, the HXD molecules most likely lie on or near the surface of the micelle because of the location of the second hydroxyl group at the end of the hexane chain. This means that there are smaller interactions of the alkyl chain with the interior of the micelle, which decreases the driving force for the HXD to enter or “to partition” into the hydrophobic interior of the micelle. $\Delta_{tr}G^0$ was calculated from the K_x values . The results in Table 3 show that upon varying the position of the second hydroxyl group (from 1,2-HXD to 1,6-HXD) $\Delta_{tr}G^0$ increases by about 3 kJ/mol in both the SDS/HXD and the DTAB/HXD mixed micelle systems. An increase in $\Delta_{tr}G^0$ indicates that the driving force for the transfer of the HXD molecule into the interior of the micelles depends greatly on the location of the hydroxyl groups on the hydrocarbon chain. It should be noted that the transfer Gibbs energy of the 1,2-HXD molecule is similar in magnitude to that of 1-butanol, indicating that the addition of the second hydroxyl group to the β carbon of the alcohol backbone increases the Gibbs transfer energy by about 5 kJ/mol, in excellent agreement with the difference in $\Delta_{tr}G^0$ between 1,2-butandiol and 1-butanol in SDS micelles [30]. For the 1,6-HXD solubilizates in the anionic and cationic micelles, we note that these p values are similar to those of 1-propanol, i.e., a monohydroxy alcohol with half the total number of carbons atoms [29].

Table 3 Partition constants (p values), mole-fraction-based distribution coefficients and Gibbs energy of transfer between the micellar phase and the aqueous phase for SDS/HXD and DTAB/HXD mixed micelle systems

Additive	p	K_x	$\Delta_{tr}G^0$/kJ/mol
SDS/1,2-HXD	0.50 ± 0.03	178 ± 13	−12.8 ± 0.2
SDS/1,6-HXD	0.20 ± 0.04	48 ± 11	−9.6 ± 0.6
DTAB/1,2-HXD	0.35 ± 0.03	142 ± 17	−12.3 ± 0.3
DTAB/1,6-HXD	0.08 ± 0.04	28 ± 13	−8.3 ± 1.3

Luminescence probing experiments

The slopes of the plots of $\ln(I_0/I)$ versus quencher concentration were used to obtain the micelle concentration in solution, $1/c_{mic}$, via the application of the Turro–Yekta equation. The surfactant aggregation numbers were calculated from [31]

$$N_s = \frac{[\text{surf}]_{mic}}{c_{mic}} \approx \frac{c_{surf,t} - \text{cmc}}{c_{mic}} \quad , \tag{8}$$

where the cmc values are those found for the mixed micelles, reported earlier. The alcohol aggregation numbers can be calculated from the following relationship, which uses the alcohol partition constants to estimate the number of alcohol molecules present in the micelle.

$$N_a = \frac{pc_{a,t}}{c_{mic}} \quad , \tag{9}$$

where $c_{a,t}$ is the concentration of the alcohol used in the system, while c_{mic} is calculated from the slope obtained from the plot of $\ln(I_0/I)$ versus quencher concentration. The surfactant and alcohol aggregation numbers for the SDS/HXD and the DTAB/HXD mixed micelles as a function of alcohol concentration are presented in Table 4. The N_s values as a function of alcohol concentration are plotted in Figs. 5 and 6 for the HXDs in SDS and DTAB micelles, respectively.

As expected, for both the SDS/1,2-HXDl and SDS/1,6-HXD mixed micelles, an increase in the alcohol concentration resulted in a decrease in the surfactant aggregation numbers. The decrease in the surfactant aggregation number (and the subsequent increase in the alcohol aggregation number) indicates that the alcohol molecules are aggregating into the micelle to a greater extent as the alcohol concentration becomes larger. Surprisingly, as shown in Figs. 5 and 6 we do not observe any significant difference in N_s for the two

Table 4 Aggregation numbers of the surfactant and alcohol for 0.0500 M SDS/1,2-HXD and 1,6-HXD mixed micelles as a function of the concentration of alcohol added $N_s \pm 3$, $N_a \pm 5$

c_a/M	SDS/1,2-HXD			SDS/1,6-HXD			DTAB/1,2-HXD			DTAB/1,6-HXD		
	N_s	N_a	N_t	N_s	N_a	N_t	N_s	N_a	N_t	N_s	N_a	N_t
0.000	67	0	67	67	0	67	51	0	51	51	0	51
0.025	59	10	69	58	3	72	48	5	53	48	1	49
0.050	56	18	74	55	5	60	47	10	57	46	2	48
0.075	53	26	79	54	8	62	44	14	58	46	2	48
0.100	48	30	78	51	9	60	40	17	57	40	4	44
0.150	45	44	89	47	13	60	36	23	59	38	5	43
0.200	40	53	93	43	16	59	32	27	59	42	7	49
0.250	34	57	91	40	18	58	–	–	–	–	–	–

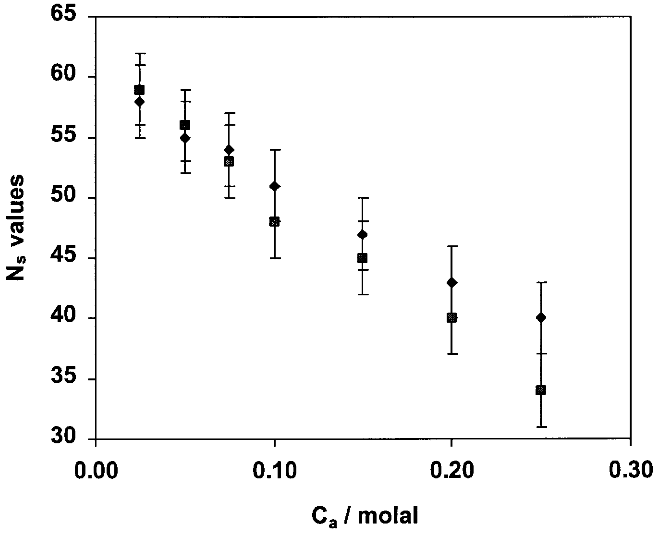

Fig. 5 Surfactant aggregation numbers versus alcohol concentration for SDS/HXD mixed micelles

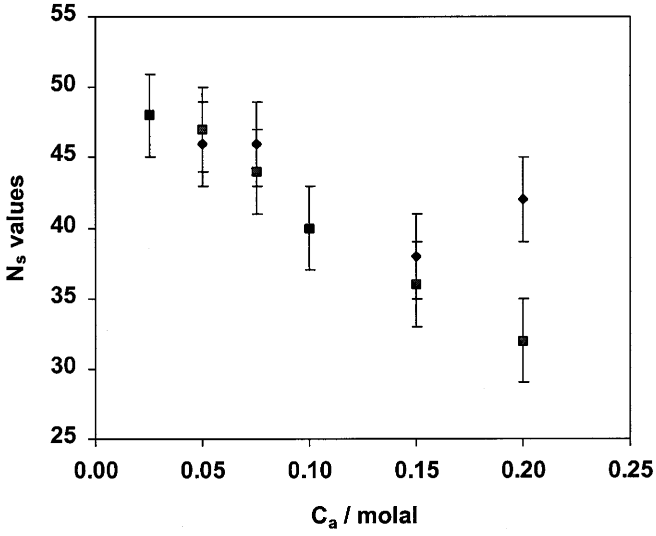

Fig. 6 Surfactant aggregation numbers versus alcohol concentration for DTAB/HXD mixed micelles

alcohol systems. If the change in N_s were due to the differences in the partition coefficients for the alcohols only, we would expect N_s to be somewhat lower for the SDS/1,2-HXD and DTAB/1,2-HXD systems than for the corresponding surfactant 1,6-HXD systems at the same alcohol concentration. Since the differences between the surfactant aggregation numbers and the α values for the surfactant/1,2-HXD systems versus the surfactant/1,6-HXD mixed micelles are small, the decrease in the chemical potential of the mixed aggregate (owing to increased van der Waals interactions) is offset by the differences in the electrostatic interactions of these alcohols in the micellar headgroup region. In fact, it appears that the placement of two hydroxyl groups on adjacent carbon atoms is not as efficient at lowering the electrostatic interactions between the surfactant headgroups as the hydroxyl groups located at both ends of the alcohol. Hence, these differences must lead to a significant contribution in the self-assembly process of these mixed micelles, as the partition coefficients indicate that there is a large difference in the Gibbs energy of transfer of the 1,2-HXD and the 1,6-HXD into the micelles.

The I_1/I_3 ratios for these systems provide information on the micropolarity of the mixed micelles. The I_1/I_3 ratios for the SDS/HXD and DTAB/HXD mixed systems are given in Table 5 as a function of the amount of alcohol added. It is apparent from the table for both

Table 5 I_1/I_3 ratios ($\pm$0.02) for SDS/HXD and DTAB/HXD mixed micelles as a function of the concentration of alcohol added

c_a/M	SDS/ 1,2-HXD	SDS/ 1,6-HXD	DTAB/ 1,2-HXD	DTAB/ 1,6-HXD
0.000	1.21	1.21	1.38	1.38
0.025	1.18	1.19	1.36	1.37
0.050	1.15	1.18	1.36	1.37
0.075	1.14	1.16	1.35	1.37
0.100	1.11	1.17	1.34	1.36
0.150	1.09	1.16	1.33	1.35
0.200	1.08	1.15	1.31	1.33
0.250	1.07	1.14	–	–

the 1,6-HXD and the 1,2-HXD that as the amount of alcohol added increases, the ratio I_1/I_3 decreases, indicating that the pyrene is sensing a less polar environment in the mixed micelles. This decrease is only slightly more significant for the surfactant/1,2-HXD mixed micelles than for the surfactant/1,6-HXD mixed micelles.

The decrease in the I_1/I_3 ratios may be explained in terms of hydration at the micellar surface. The presence of the alcohol molecules in the micelle blocks the penetration of the water into the mixed micelles and, therefore, the probe senses a less polar environment. As the alcohol concentration in the mixed solvent is increased, the probe molecules should sense a less polar environment, as more water is expelled form the surface of the mixed micelles. On the basis of the values of *p* obtained from the NMR–PRE experiments, a significant difference in the I_1/I_3 ratios between the surfactant/1,2-HXD systems and the surfactant/1,6-HXD systems is expected as there is a significant difference in the partition coefficients of the alcohols in both ionic micellar systems. This was observed by Marangoni et al. [32] in their work on surfactant/alkoxyethanol mixed micelles. However, this is indeed not the case when we examine the data from Table 5, which may again be due to the manner in which the 1,6-HXD screens (shields) the electrostatic interactions in the micellar headgroup region compared to the 1,2-HXD.

Conclusions

From the conductance, luminescence probing and NMR–PRE experiments, we conclude that the addition of the isomeric HXDs to the mixed solvents causes a change in the micellar properties of the host surfactant systems. The cmc values indicate that these alcohols contribute to both the electrostatic and hydrophobic parts of the Gibbs energy of micelle formation. In examining the partition coefficients, we see fairly large differences in the amount of alcohol that penetrates the micellar phase, which would explain the differences in the cmc values. However, the degrees of counterion dissociation and the N_s values indicate that the positioning of the two hydroxyl groups on adjacent carbon atoms (1,2-HXD) may not be as effective in reducing the electrostatic interactions between the charged surfactant headgroups as for the 1,6-HXD. This is evidenced by the fact that the α values and the N_s values are not very different between the surfactant/1,2-HXD mixed micelles and the surfactant/1,6-HXD mixed micelles at the same concentration of alcohol, even though the partition constants indicate that the 1,2-HXD is preferentially solubilized in the micellar phase. It appears, therefore, that the position of the hydroxyl groups on the alcohol chain makes a significant contribution to both hydrophobic and electrostatic aspects of the self-assembly process.

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