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ORIGINAL CONTRIBUTION

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The partitioning of alkanediols into SDS and DTAB micelles from NMR-PRE experiments

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Abstract The *p*-values of a number of α,ω-alkanediols, 1,2-alkanediols, and 1,5-hexanediol and 2,5-hexanediol between D_2O and the micellar phases of anionic sodium dodecylsulfate (SDS) and cationic dodecyltrimethylammonium bromide (DTAB) have been determined using the using a NMR paramagnetic relaxation enhancement experiment (NMR-PRE). From the *p*-values, mole-fraction based partition coefficients and Gibbs energies of transfer for the alkanediols from the bulk D_2O phase to the micellar phase have been calculated. Differences in the partition coefficients of the α,ω-alkanediols and the 1,2-alkanediols are discussed in terms of the smaller Gibbs transfer energy per CH_2 group for α,ω-alkanediols. For the 1,5- and the 2,5-hexanediols, the *p*-values are substantially smaller than for the other hexanediols in both SDS and DTAB micelles. All of these results are consistent with the location of the two hydroxyl groups on the carbon backbone making a substantial contribution to the thermodynamics of transfer of solubilizates.

Keywords Mixed micelles · Alkanediols · Surfactants · NMR · Partition constants

Introduction

The physico-chemical properties of surfactant micelles are altered when water-soluble additives like alcohols, alkanediols, and amines [1] are either dissolved in the micelle interior or form a mixed solvent system with water. In the case of micellar dissolved additives, a key parameter in understanding the fundamental properties of mixed micellar systems is the *p*-value, which is defined as follows

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

where $c_{\mathrm{a,mic}}$ is the concentration of solubilizate (additive) in the micellar phase and $c_{\mathrm{a,t}}$ represents the total concentration of additive [2]. The degree of solubilization of alcohols in mixed micelles has been obtained using many different methods [3, 4, 5, 6]. NMR measurements of solubilization are usually accomplished via a Nuclear Magnetic Resonance (NMR) Paramagnetic Relaxation Experiment [4, 7], or by the NMR Fourier-Transform Pulsed Gradient Spin Echo experiment developed by Stilbs [8, 9, 10].

There have only been a few papers that have dealt with the solubilization of branched or non-primary alcohols or alkanediols [8, 10, 11, 12]. For example, Stilbs examined the solubilization of a number of non-primary alcohols like 2- and 3-pentanol and branched alcohols (like *t*-pentyl alcohol) in SDS micelles, and found that the *p*-value decreased as the degree of branching of the hydrocarbon chain increased or as the hydroxyl group was placed closer to the centre of the hydrocarbon chain. In addition, it is well known that when alcohols are solubilized in micellar solutions, the hydroxyl group will be located in the micellar palisade layer with the hydrocarbon chain interacting with the hydrophobic groups in the micelle interior. Hence, when the hydroxyl group is located near the centre of a short hydrocarbon chain, as is the case with 2-pentanol, 3-pentanol, 3-heptanol and 4-heptanol, these alcohols will be solubilized mainly near the surface of the micelle, whereas the alkyl chain of an *n*-alcohol interacts with those parts of the hydrocarbon chains located more deeply in the micellar interior.

The purpose of the present work was to investigate the solubilization of a series of α,ω-alkanediols, 1,2-hexanediols, and some substituted hexanediols in the interior of SDS and DTAB micelles. The *p*-values have been determined from a NMR-PRE experiment. These surfactants have been chosen on the basis that they represent typical anionic and cationic surfactants, and there is a wealth of distribution coefficient data for alcohols of various types in these systems [10, 13]. The $\Delta_{tr}G^\circ$ values, the Gibbs energies of transfer of the alcohols from the D_2O phase to the micellar phase, have been calculated from the distribution coefficients. The results are discussed in terms of the variations in the distribution coefficients of the α,ω-alkanediols versus the 1,2-alkanediols due to the differences in the entropic contributions to the $\Delta_{tr}G^\circ$ values. For the 1,5- and the 2,5-hexanediols, the differences in the *p*-values between these and other hexanediols are interpreted in terms of the contribution of the location of the two hydroxyl groups on the carbon backbone to the thermodynamics of transfer of the solubilizate.

Experimental

Materials

Sodium dodecyl sulfate (SDS) was obtained from OmniPur at 99% purity. The dodecyltrimethylammonium bromide (DTAB) was obtained from Sigma-Aldrich and was purified by repeated recrystallization in an acetone/ethanol mixture, followed by treatment with decolourizing charcoal. All alkanediols used in the present work were obtained from Aldrich or Fluka at a minimum of 95% purity, and were used without further purification. The spin-lattice relaxation times (T_1 values) were measured on freshly prepared solutions, using the methods and techniques discussed previously [4, 11, 12]. The errors in the T_1 values, estimated from reproducibility of the T_1's in separate trials, were used to obtain the error estimates in the calculated *p*-values, distribution coefficients, and Gibbs energies.

Results and discussion

The degree of solubilization, *p*, of the alkanediol molecules in SDS and DTAB micelles can be obtained from NMR spin-lattice relaxation rate measurements using the equation [14]:

$$p = 1 - \frac{R_1^p(\text{obs}) - R_1(\text{obs})}{R_1^p(\text{aq}) - R_1(\text{aq})} \tag{2}$$

where $R^p{}_1(\text{obs})$ and $R_1(\text{obs})$ are the spin-lattice relaxation rates for the alkanediol solubilizates in micellar solution in the presence and absence of paramagnetic ions, respectively. $R^p{}_1(\text{aq})$ and $R_1(\text{aq})$ are the relaxation rates of the alkanediol additives in aqueous solution in the presence and absence of paramagnetic ions, respectively ($R_1 = 1/T_1$). From the measured *p*-values, we have calculated the mole fraction-based distribution coefficients, the K_x values, for all the alcohols in SDS and DTAB micelles:

$$K_X = \frac{X_{\text{mic}}}{X_{\text{aq}}} \tag{3}$$

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

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

$$X_{\text{aq}} = \frac{(1-p)c_{\text{a,t}}}{c_{\text{D}_2\text{O}}} \tag{5}$$

where $c_{\text{surf,t}}$ and $c_{\text{surf,mon}}$ are the total and the monomeric concentrations of surfactant, respectively; c_{D2O} is the solvent concentration and $c_{\text{a,t}}$ is the additive concentration in molar units. The Gibbs energy of transfer of the alcohol from the aqueous phase to the micellar phase (the $\Delta_{tr}G^\circ$ value) is obtained from the standard thermodynamic relationship

$$\Delta_{\text{tr}}G^{\text{o}} = -RT\ \ln K_x \tag{6}$$

Tables 1 and 2 present the data for the *p*-values of all the alkanediols investigated in SDS and DTAB micelles, respectively. We note that the measured values of the *p*-values for 1,2- and 1,6-hexanediol in SDS and DTAB micelles and 1,2- and 1,4-butanediol in SDS micelles are in excellent agreement with our previous papers [11, 12]. As expected, for both the SDS and the DTAB systems, we note that increasing the chain length of the alkanediols substantially increases their partition coefficients, as previously seen in the literature with other additive systems as a function of alcohol chain length [4, 8, 13]. In all cases, we observe that the 1,2-alkanediols partition into the SDS and DTAB micelles to a greater degree than the α-ω-alkanediols, in excellent agreement with our previous paper [11] and that of Stilbs [10]. In Figs. 1 and 2, the partition coefficients for the 1,2-alkanediols

Table 1 P-values, mole fraction-based distribution coefficients and Gibbs energies of transfer between the micellar and aqueous phases for SDS/alkanediol systems

Additive	*p*	K_x	$\Delta_{tr}G^\circ$ (kJ/mol)
1,2-butanediol	0.08 ± 0.05	19 ± 12	−7.3 ± 1.5
1,2-pentanediol	0.15 ± 0.05	35 ± 13	−8.8 ± 0.9
1,2-hexanediol	0.50 ± 0.03	178 ± 19	−12.8 ± 0.3
1,2-octanediol	0.87 ± 0.01	1245 ± 76	−17.6 ± 0.2
1,2-decanediol	0.98 ± 0.01	9194 ± 2085	−22.5 ± 0.6
1,4-butanediol	0.06 ± 0.04	13 ± 13	−6.4 ± 2.0
1,6-hexanediol	0.25 ± 0.04	65 ± 13	−10.3 ± 0.5
1,7-heptanediol	0.51 ± 0.03	158 ± 18	−12.5 ± 0.3
1,8-octanediol	0.70 ± 0.02	364 ± 27	−14.6 ± 0.2
1,10-dedcanediol	0.93 ± 0.01	2098 ± 154	−18.9 ± 0.2
1,5-hexanediol	0.10 ± 0.04	22 ± 11	−7.6 ± 1.2
2,5-hexanediol	0.05 ± 0.04	12 ± 10	−6.1 ± 2.2

Table 2 P-values, mole fraction-based distribution coefficients, and Gibbs energies of transfer between the micellar and aqueous phases for DTAB/alkanediol systems

Additive	*p*	K_x	$\Delta_{tr}G^\circ$ (kJ/mol)
1,2-butanediol	0.04 ± 0.03	13 ± 13	−6.5 ± 2.3
1,2-pentanediol	0.12 ± 0.03	43 ± 14	−9.3 ± 0.8
1,2-hexanediol	0.33 ± 0.03	139 ± 17	−12.2 ± 0.3
1,2-octanediol	0.82 ± 0.01	1243 ± 55	−17.6 ± 0.3
1,2-decanediol	0.96 ± 0.01	6021 ± 862	−21.5 ± 0.4
1,4-butanediol	0.03 ± 0.03	11 ± 11	−6.0 ± 2.9
1,6-hexanediol	0.15 ± 0.03	53 ± 14	−9.8 ± 0.6
1,7-heptanediol	0.37 ± 0.02	136 ± 17	−12.1 ± 0.3
1,8-octanediol	0.59 ± 0.02	333 ± 24	−14.4 ± 0.2
1,10-dedcanediol	0.88 ± 0.01	1813 ± 84	−18.5 ± 0.1
1,5-hexanediol	0.07 ± 0.04	26 ± 17	−8.0 ± 1.5
2,5-hexanediol	0.06 ± 0.04	22 ± 16	−7.6 ± 1.8

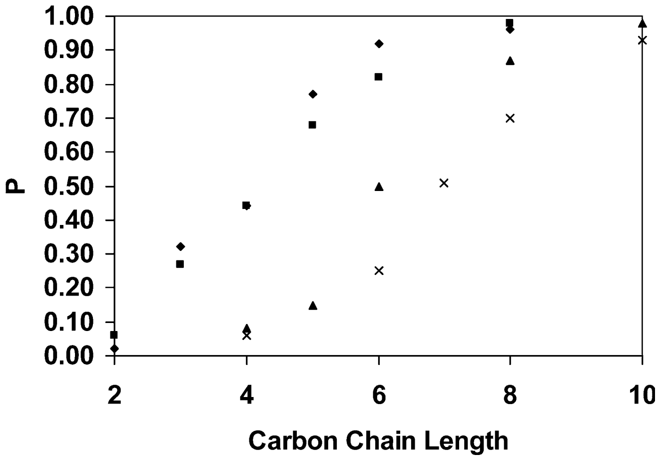

Fig. 1 *P*-values of alcohols and alkanediols in SDS micelles. Diamonds: *n*-alcohols (from Stilbs [8]); squares: *n*-alcohols (from Marangoni and Kwak [13]); triangles: 1,2-alkanediols; x's: α,ω-alkanediols

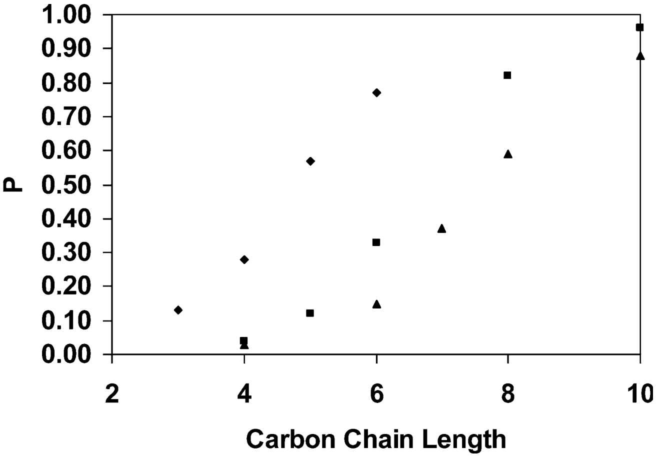

Fig. 2 *P*-values of alcohols and alkanediols in DTAB micelles. Diamonds: *n*-alcohols (from Gao et al [21]); squares: 1,2-alkanediols; triangles: α,ω-alkanediols

and the α,ω-alkanediols in SDS micelles are plotted and compared to the *p*-values for the *n*-alcohols determined using the NMR-PRE experiment [13] and the FT-PGSE experiment [8]. We can clearly see that the *p*-values for all of the substituted alkanediols are smaller than those of their monohydroxy analogues, as expected, indicating that the driving force for the transfer of the diols from the D_2O phase to the micellar phases of SDS and DTAB is clearly diminished. In almost all cases, the *p*-values of the α,ω-alkanediols are comparable to the corresponding *n*-alcohol containing half the total number of carbon atoms, whereas for the 1,2-alkanediols, the *p*-values are comparable to an *n*-alcohol with two fewer carbon atoms. The calculated values for the distribution coefficients (K_x values) and the Gibbs transfer energies ($\Delta_{tr}G^\circ$ values) are also presented in Tables 1 and 2, respectively. If we examine the Gibbs transfer energies in the tables, we clearly see differences in the driving forces for the transfer of the additives from the aqueous phase to the micellar phase between the α,ω-alkanediols versus those of the 1,2-alkandiols, in excellent agreement with our previous paper [11]. It appears that placing the hydroxyl groups in the α,ω-position versus the 1,2 position decreases the driving force for their solubilization by about 3 kJ/mol on average, with the difference appearing to increase slightly as the alkanediol chain length increases.

If we plot the $\Delta_{tr}G^\circ$ values as a function of the number of carbons in the alcohol, the slope is proportional to the transfer Gibbs energy of the CH_2 groups from the aqueous phase to the micellar phase. These plots are presented in Figs. 3 and 4 for alkanediols in SDS and DTAB micelles, respectively. The Gibbs transfer energy increment per CH_2 group is 2.6 ± 0.30 kJ/mol for the 1,2-alkanediols and 2.1 ± 0.2 kJ/mol for the α,ω-alkanediols into SDS micelles, respectively. We calculate the $\Delta_{tr}G^\circ/CH_2$ group

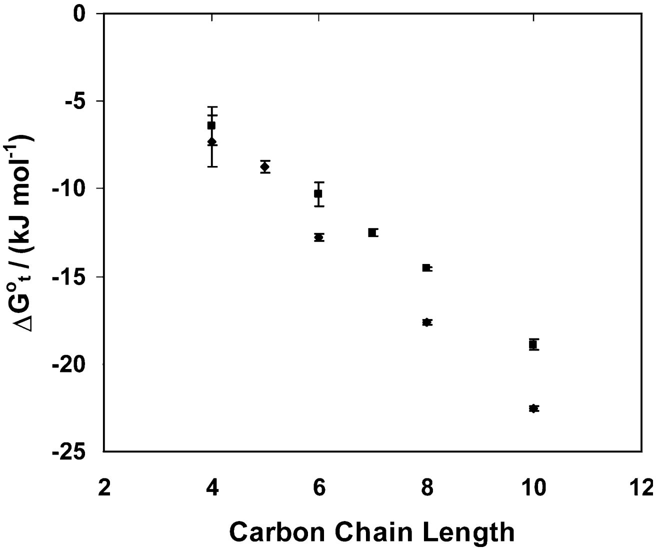

Fig. 3 Gibbs transfer energies for 1,2-alkanediols (diamonds) and α,ω-alkanediols (squares) into the SDS micelles phase as a function of the carbon chain length

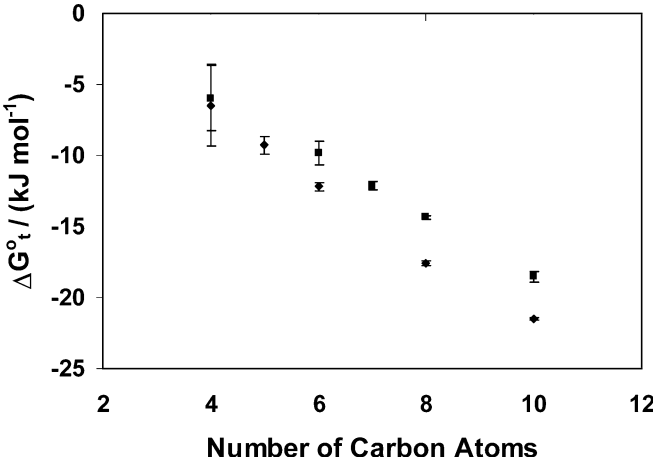

Fig. 4 Gibbs transfer energies for 1,2-alkanediols (diamonds) and α,ω-alkanediols (squares) into the DTAB micelles phase as a function of the carbon chain length

values for the 1,2-alkanediols and the α,ω-alkanediols into the interior of the DTAB micelles to be 2.5 ± 0.3 kJ/mol and 2.1 ± 0.2 kJ/mol, respectively. The slightly lower value of the $\Delta_{tr}G°/CH_2$ in the case of the α,ω-alkanediols appears to indicate some difficulty in additional CH_2 groups penetrating the micellar interior and contributing to hydrophobic interactions. We expect that the most likely locus of solubilization for the α,ω-alkanediols would be in the micelle palisade layer region; they would adopt a wicket-like configuration much like the conformations adopted by bolaform surfactants when they form micelles or are adsorbed at the air-water interface [15, 16, 17, 18, 19]. The adoption of this wicket-like configuration will decrease the entropy of transfer ($\Delta_{tr}S°$) per CH_2 group, leading to less negative $\Delta_{tr}G°$ values. This is consistent with the high order parameters and fast motion correlation times observed for bolaform surfactants in aqueous solution [20]. In the case of the 1,2-alkanediols, we would expect them to adopt a configuration in the micelle similar to that of the *n*-alcohols; hence, we observe that the $\Delta_{tr}G°/CH_2$ group is similar to the value reported by Marangoni and Kwak [13] and by Stilbs [8].

For the 1,5-hexanediol and the 2,5-hexanediol systems, we note that the *p*-values for these diols in both SDS and DTAB micelles are much lower for than for the other hexanediols in these micelles, again indicating that the degree of solubilization is dependent on the position of the hydroxyl groups on the hydrocarbon chain, in excellent agreement with Stilbs [8] and our previous work [11]. Those data are not of sufficient precision to determine whether or not the solubilization of the 1,5-hexanediol is preferred over that of the 2,5-hexanediol in the micellar interior or vice versa. However, we clearly see in both cases that moving the hydroxyl group towards the centre of the alkyl chain results in a 2–3 kJ/mol reduction in the $\Delta_{tr}G°$ values versus either the 1,2-hexanediol or the 1,6-hexanediol. This reduction in the Gibbs energy is again likely due to the significant entropy cost in anchoring the molecules in the micelle palisade layer region. It appears that within the error limits of the measurements reported above that the entropic penalty is similar for the both the 2,5- and the 1,5-HXD molecules. Somewhat more surprising is the fact that the *p*-values of these diols are the same as the 1,4-BTD in both micellar systems. This indicates that the entropic reduction due the anchoring effect of the hydroxyl groups in the headgroup region may indeed be larger for the diols with the -OH groups closer to the chain centre. For both alcohols then, it is likely that the placement of the hydroxyl groups towards the middle of the chain leads to a substantial decrease in the entropy of transfer, due to the loss of rotational freedom as the alcohol headgroups are anchored in the palisade layer region.

Conclusions

From the partition coefficients obtained via NMR-PRE experiments, we conclude that the degree of solubilization for a series of 1,2-alkanediols and α,ω-alkanediols increases with an increase in the number of CH_2 groups in the alkanediols, as expected. However, we observe differences in the amount of alcohol that penetrates the micellar phase between the 1,2-alkanediols and the α,ω-alkanediols of the same chain length. In addition, it appears that the $\Delta_{tr}G°/CH_2$ groups is different for the two homologous series, which is attributed to a decrease in the $\Delta_{tr}S^{\circ}/CH_2$ group for the α,ω-alkanediols versus the 1,2-hexanediols. Finally, the *p*-values for both 1,5-hexanediol and 2,5-hexanediol are diminished versus the other hexanediols studied in this paper. This is consistent with a reduction in the Gibbs transfer energy of the alcohol as the hydroxyl group is placed near the centre of the hydrocarbon chain, which is likely due to the loss of entropy as the alcohol groups become more anchored in the micelle palisade layer.

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