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Micellar Properties and Related Thermodynamic Parameters of Aqueous Anionic Surfactants in the Presence of Monohydric Alcohols

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S *Supporting Information*

ABSTRACT: The effect of monohydric alcohols, (C_7-C_{10}), on the micellar behavior of anionic surfactants, sodium dodecylsulfate (SDS) and sodium dodecylbenzene sulfonate (SDBS), was investigated using experimentally measured densities, ρ, speeds of sound, u, and specific conductivities, κ, at various temperatures and atmospheric pressure. A number of thermodynamic parameters, like apparent molar volumes, Φv, partial molar volumes, $\Phi^{\circ} v$, isentropic compressibility, κ_s, and various thermodynamic parameters of micellization were calculated to elucidate the interactions prevailing in the studied aqueous surfactant−alcohol systems. The decrease in critical micelle concentration (cmc) on addition of an additive may be seen in terms of establishment of additional hydrophobic interactions between the hydrophobic part of the surfactant and additive molecules. It can be seen that $\Delta G^{\circ}_{m} < 0$ is weakly dependent on alcohol concentrations in aqueous surfactant solutions. Further, ^{1}H and ^{13}C NMR chemical shift measurements in micelle solutions containing above-mentioned alcohols have also been carried out. From ^{1}H and ^{13}C NMR spectra, it was concluded that the site for preferential solubilization of alcohol is close to the headgroup of the micelle. The trend observed in carbon chemical shifts may be attributed to the chain length of the added alcohols due to the strong ion−dipole interaction between the negatively charged SDS headgroup and the hydroxyl group of the alcohol.

INTRODUCTION

The solubilization of polar molecules, such as alcohols, in aqueous surfactant systems is quite complex. However, being confined to the aqueous micellar phase, polar solutes are generally found to solubilize in micelles with the polar group anchored in the headgroup region. If the hydrocarbon chain of the polar compound is sufficiently long, it will presumably extend to the micellar core.[1] Zana[2] suggested that the number of polar solutes anchored in the headgroup region is limited. From solubility measurements, it has been observed that the amount of alcohol solubilized per amphiphile molecule can be significantly larger, which suggests that the alcohol molecules will penetrate deeper into the micelle.[3] The effect of alcohols on the self-association processes of ionic surfactants and hence on the properties of the micelles formed has been investigated for several systems using a variety of techniques.[4−8] The addition of alcohol can strongly influence the behavior of the micelles and increase or decrease the micellar size depending on the hydrophilic/hydrophobic character of the alcohol.[6] The hydrophobic alcohol molecules take part in the micellization process and become unique components of the micelle aggregates.

The surfactants undertaken for the present studies are sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (SDBS). SDS is a much-investigated anionic surfactant, whereas very few data in literature are available on the solution properties of SDBS.[9−12] While the reports on the interaction of SDS with alcohols are considerable,[4−8,13] those with SDBS are quite limited.[14]

In continuation of my previous work,[6,14] the present paper reports the effect of monohydric alcohols, heptan-1-ol, octan-1-ol, nonan-1-ol, and decan-1-ol, on the micellization behavior of anionic surfactant SDS, using density and speed of sound measurements at temperatures between (298.15 and 308.15) K. Apart from these, ^{1}H and ^{13}C NMR studies have also been carried out for the above-mentioned SDS−alcohol systems. Conductometric measurements were made for the surfactant SDS in the presence of octan-1-ol at temperatures between (298.15 and 313.15) K. However, volumetric studies were made for the surfactant SDBS in the presence of heptan-1-ol. Thermodynamic parameters, like the apparent molar volumes, Φv, partial molar volumes, $\Phi^{\circ} v$, isentropic compressibility, κ_s, and various thermodynamic parameters of micellization, were calculated from experimental data to elucidate the interactions prevailing in the studied aqueous surfactant−alcohol systems. Further, the results obtained from ^{1}H and ^{13}C NMR chemical shift measurements in micelle solutions containing the above-mentioned alcohols are discussed in light of the conclusions drawn from the thermodynamic measurements.

EXPERIMENTAL SECTION

Materials. SDS was obtained from HiMedia Laboratories Pvt. Ltd., Mumbai, India and was purified by the method suggested in the literature.[15] SDBS (mass fraction purity of 0.88) was purchased by Acros Organics (New Jersey). It was purified by the method given by Alauddin et al.[10] The purified product was dried under vacuum in the presence of P_2O_5 for few days. The expected mass fraction purity of the recrystallized SDBS was >0.97 as checked by comparing the data of critical micelle concentrations of aqueous SDBS given by Hait et al.[9] The experimental values of

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Table 1. Comparison of Experimental Density, ρ, and Speed of Sound u, of Pure Liquids with Literature Data

		$\rho \cdot 10^{-3}/\text{kg} \cdot \text{m}^{-3}$		$u/\text{m} \cdot \text{s}^{-1}$	
alcohol	T/K	exptl	lit.	exptl	lit.
heptan-1-ol	298.15	0.819398	0.8190[a] o.8199[a]	1328.1	-
	303.15	0.815848	0.8160[a]	1311.2	1311.0[d]
	308.15	0.812279	0.8126[b]	1294.5	-
octan-1-ol	298.15	0.821748	0.82157[c]	1347.4	1348.0[e]
	303.15	0.818263	0.8184[e]	1330.6	1332.1[d]
	308.15	0.814764	0.8150[e]	1313.9	1314.27[e]
nonan-1-ol	298.15	0.824811	0.8246[d]	1364.5	1364.34[f]
	303.15	0.821349	-	1347.6	1350.0[f]
	308.15	0.817876	-	1331.0	-
decan-1-ol	298.15	0.827780	0.82676[d]	1380.68	1380.01[g]
	303.15	0.824327	0.8230[b]	1363.5	1363.1[g]
	308.15	0.820859	0.8194[b]	1346.68	1346.3[g]

[a] Reference 16. [b] Reference 17. [c] Reference 18. [d] Reference 19. [e] Reference 20. [f] Reference 21. [g] Reference 22.

speed of sound at 298.15 K for aqueous SDBS were compared with that reported in literature.[10] The analytical grade octan-1-ol (mass fraction purity 0.99) was obtained from Spectrochem Pvt Ltd. Mumbai, India, whereas heptan-1-ol, nonan-1-ol, and decan-1-ol were Aldrich products of mass fraction purity >0.98. Alcohols were purified by fractional distillation before use. The purity of these liquids was ascertained by comparing their measured densities, ρ, and speeds of sound, u, with the available literature shown in Table 1 as well as from the ^{1}H NMR studies. The standard uncertainties in density measurements were estimated to be $\pm\, 2 \cdot 10^{-3}$ kg$\cdot$m^{-3} and for the speed of sound $\pm$ 0.1 m$\cdot$s^{-1} and were compared with that reported in the literature.[16−22] Deuterium oxide purchased from Aldrich (mass fraction purity >0.99) was used without further purification as a solvent in ^{1}H NMR and ^{13}C studies. Deionized, double-distilled water of conductance $1 \cdot 10^{-6}$ S$\cdot$cm^{-1} at 298.15 K was used for all of the measurements. The solutions were prepared by weighing an appropriate amount of the surfactant on an electronic balance (Afcoset-ER120A) with a precision of 0.0001 g. Bidistilled water and alcohols were degassed by vacuum pump shortly before sample preparation. Details have been given in my previous communications.[6,14]

Apparatus and Procedure. All samples were stored in dark bottles over a freshly activated molecular sieve (Ranbaxy 3A^0 × 1.5 mm pellets) to minimize the adsorption of moisture. Measurements of the density, ρ, and the speed of sound, u, of pure liquids and their solutions were carried out using a digital vibrating-tube densimeter and speed of sound analyzer (Anton Paar DSA-5000) provided with automatic viscosity correction and two integrated Pt 100 Ω thermometers. The temperature in the cell was regulated ± 0.001 K with a proportional temperature controller. The apparatus was first calibrated with triple-distilled water and dry air.

Conductivities were measured using digital conductivity meter (306) of Systronics which is a microcontroller based instrument for measuring specific conductivity of solutions using a conductivity cell. The accuracy in conductance measurements is ± 1 %. The conductivities were determined at (298.15, 303.15, 308.15, and 313.15) K. Measurements were carried out in a jacket containing conductivity cell of cell constant 1.0 ± 0.1 cm^{-1}. Water was circulated in the jacket from thermostat and the temperature was maintained within ± 0.01 K. The data of specific conductance is given in Supporting Information. The critical micelle concentration, cmc, of SDS in an aqueous solution was taken as the break point in the plot of specific conductance vs. molar concentration (mol$\cdot$dm^{-3}) of SDS. However, in the present paper cmc is expressed in mole fraction unit and is presented as x_{cmc} whereas a molar concentration of alcohol is denoted by M.

To investigate the effect of alcohols on micellar phase of SDS, ^{1}H NMR as well as ^{13}C NMR measurements were performed on Bruker 300 NMR spectrometer at frequency 300.13 (^{1}H) and 75.47 (^{13}C) MHz, respectively. Deuterium oxide was used as the solvent instead of water to weaken the water signal for all solutions. The internal reference is tetramethylsilane (TMS). Because all 12 hydrogen atoms in a TMS molecule are equivalent, its ^{1}H NMR spectrum consists of a singlet. The chemical shift of this singlet is assigned as δ 0, and all other chemical shifts are determined relative to it. Similarly, all four carbon atoms in a TMS molecule are equivalent. In a fully decoupled ^{13}C NMR spectrum, the carbon in the TMS appears as a singlet, allowing for easy identification. The chemical shift of this singlet is also set to be δ 0 in the ^{13}C spectrum, and all other chemical shifts are determined relative to it. In the present NMR studies, the method depends on the ability of the alcohols to affect the chemical shift of different proton and carbon signals of the surfactant molecules. ^{1}H and ^{13}C spectra of 0.1 mol$\cdot$kg^{-1} surfactant solutions were obtained in the absence and in the presence of studied monohydric alcohols. The chemical shift differences were only considered in this study. The chemical shift measurements of various resonance peaks of SDS are given on the δ scale in parts per million (ppm). Further information about the experimental techniques has been provided in literature.[8,14]

RESULTS AND DISCUSSION

The experimental data of density, ρ, and speed of sound, u, along with the apparent molar volume (Φv) in the case of aqueous 0.10 mol$\cdot$kg^{-1} SDS/SDBS with heptan-1-ol at (298.15, 303.15, and 308.15) K and atmospheric pressure are reported in Table 2. The above mentioned experimental measurements for (0.05 and 0.10) mol$\cdot$kg^{-1} SDS solutions in the presence of octan-1-ol are reported in Table 3, whereas those in the case of 0.10 mol$\cdot$kg^{-1} SDS solution with nonan-1-ol and decan-1-ol are presented in Table 4. The uncertainty reported in density measurements is $\pm\, 2 \cdot 10^{-3}$ kg$\cdot$m^{-3} and in the speed of sound is ± 0.1 m$\cdot$s^{-1}. In the case of solutions containing alcohols, a close inspection of the density data from Tables 2 to 4 suggest a small change in the slope of density versus alcohol concentration, which gives a slight increase in apparent molar volumes.

The apparent molar volumes of aqueous SDS solutions as well as that of alcohols in aqueous SDS solutions can be calculated from the density data using the following expression:

$$\Phi v = (M/\rho) - [\{1000(\rho_o - \rho)\}/m\rho\rho_o] \qquad (1)$$

where ρ_o, M, and m are, respectively, the density of the pure solvent, the molar mass of the solute, and the molality of the solution in mol$\cdot$kg^{-1}. The expanded uncertainty of apparent molar volumes in the studied solutions is ± 0.3 cm^3$\cdot$mol^{-1}. The partial molar volumes, $\Phi^\circ v$, at infinite dilution of the alcohols in aqueous micelle solution were determined by using the least-squares method to the assumed relation:

$$\Phi v = \Phi^\circ v + S_v m \qquad (2)$$

Table 2. Density, ρ, Speed of Sound, u, and Apparent Molar Volume, Φv, of Heptan-1-ol in Aqueous Surfactant Solutions (0.10 mol·kg^{-1}) at (298.15, 303.15, and 308.15) K

m	$\rho\cdot10^{-3}$	u	Φv	$\rho\cdot10^{-3}$	u	Φv	$\rho\cdot10^{-3}$	u	Φv
mol·kg^{-1}	kg·m^{-3}	m·s^{-1}	cm^3·mol^{-1}	kg·m^{-3}	m·s^{-1}	cm^3·mol^{-1}	kg·m^{-3}	m·s^{-1}	cm^3·mol^{-1}
				SDS + Heptan-1-ol					
	298.15 K			303.15 K			308.15 K		
0.000	1.000966[a]	1498.0	-	0.999555	1509.5	-	0.997734[a]	1519.1	-
0.012	1.000688	1497.8	138.69	0.999270	1509.2	139.48	0.997445	1518.7	140.11
0.028	1.000324	1497.6	138.86	0.998898	1508.8	139.58	0.997068	1518.1	140.20
0.034	1.000187	1497.5	138.91	0.998758	1508.6	139.62	0.996926	1517.9	140.24
0.042	1.000006	1497.4	138.97	0.998573	1508.4	139.68	0.996739	1517.6	140.29
0.051	0.999806	1497.2	139.04	0.998369	1508.1	139.74	0.996532	1517.2	140.36
0.062	0.999545	1497.0	139.13	0.998102	1507.8	139.84	0.996261	1516.8	140.46
0.075	0.999252	1496.7	139.24	0.997805	1507.5	139.91	0.995959	1516.3	140.55
				SDBS + Heptan-1-ol					
0.000	1.002755[b]	1500.0	-	1.001200	1511.9	-	0.999440[b]	1523.4	-
0.011	1.002503	1499.6	138.10	1.000942	1511.4	138.87	0.999175	1523.0	139.78
0.022	1.002263	1499.2	138.20	1.000696	1511.0	139.00	0.998923	1522.5	139.88
0.035	1.001970	1498.8	138.30	1.000396	1510.5	139.09	0.998614	1521.9	140.01
0.048	1.001675	1498.3	138.41	1.000093	1510.0	139.22	0.998301	1521.3	140.18
0.053	1.001561	1498.2	138.45	0.999975	1509.7	139.29	0.998180	1521.1	140.24
0.061	1.001379	1497.9	138.52	0.999790	1509.4	139.33	0.997990	1520.7	140.28
0.072	1.001124	1497.5	138.60	0.999530	1508.9	139.40	0.997720	1520.2	140.39

[a] Data taken from ref 6. [b] Data taken from ref 14.

Table 3. Density, ρ, Speed of Sound u, and Apparent Molar Volume, Φv, of Octan-1-ol in Aqueous SDS Solutions (0.05 and 0.10 mol·kg^{-1}) at (298.15, 303.15, and 308.15) K

m	$\rho\cdot10^{-3}$	u	Φv	$\rho\cdot10^{-3}$	u	Φv	$\rho\cdot10^{-3}$	u	Φv
mol·kg^{-1}	kg·m^{-3}	m·s^{-1}	cm^3·mol^{-1}	kg·m^{-3}	m·s^{-1}	cm^3·mol^{-1}	kg·m^{-3}	m·s^{-1}	cm^3·mol^{-1}
				(0.05 mol·kg^{-1}) SDS + Octan-1-ol					
	298.15 K			303.15 K			308.15 K		
0.000	0.999078	1498.3	-	0.997652	1510.1	-	0.995942	1520.2	-
0.007	0.998896	1498.0	156.47	0.997463	1509.8	157.69	0.995745	1519.8	159.16
0.010	0.998815	1497.9	156.49	0.997379	1509.7	157.64	0.995658	1519.7	159.15
0.012	0.998758	1497.8	156.51	0.997320	1509.6	157.75	0.995596	1519.6	159.18
0.017	0.998635	1497.7	156.53	0.997192	1509.4	157.80	0.995464	1519.3	159.18
0.024	0.998450	1497.4	156.58	0.996999	1509.1	157.86	0.995263	1519.0	159.27
0.027	0.998366	1497.3	156.59	0.996912	1508.9	157.89	0.995173	1518.8	159.28
0.035	0.998164	1497.0	156.65	0.996702	1508.6	157.96	0.994955	1518.4	159.35
0.038	0.998088	1496.9	156.68	0.996622	1508.5	158.00	0.994872	1518.3	159.39
				(0.01 mol·kg^{-1}) SDS + Octan-1-ol					
0.000	1.000966	1498.0	-	0.999555	1509.5	-	0.997734	1519.1	-
0.008	1.000744	1497.8	156.52	0.999326	1509.2	157.61	0.997495	1518.7	159.14
0.010	1.000696	1497.7	156.62	0.999277	1509.1	157.61	0.997444	1518.7	159.13
0.012	1.000640	1497.7	156.67	0.999219	1509.1	157.68	0.997384	1518.6	159.17
0.021	1.000397	1497.4	156.78	0.998967	1508.7	157.88	0.997120	1518.1	159.45
0.023	1.000340	1497.3	156.84	0.998908	1508.6	157.95	0.997059	1518.1	159.49
0.026	1.000270	1497.3	156.88	0.998835	1508.5	158.01	0.996984	1517.9	159.51
0.033	1.000074	1497.0	157.03	0.998633	1508.2	158.15	0.996773	1517.6	159.67

Table 4. Density, ρ, Speed of Sound, u, and Apparent Molar Volume, Φv, of Nonan-1-ol and Decan-1-ol in Aqueous SDS Solutions ($0.10\ \text{mol}\cdot\text{kg}^{-1}$) at (298.15, 303.15, and 308.15) K

m / $\text{mol}\cdot\text{kg}^{-1}$	$\rho\cdot10^{-3}$ / $\text{kg}\cdot\text{m}^{-3}$	u / $\text{m}\cdot\text{s}^{-1}$	Φv / $\text{cm}^3\cdot\text{mol}^{-1}$	$\rho\cdot10^{-3}$ / $\text{kg}\cdot\text{m}^{-3}$	u / $\text{m}\cdot\text{s}^{-1}$	Φv / $\text{cm}^3\cdot\text{mol}^{-1}$	$\rho\cdot10^{-3}$ / $\text{kg}\cdot\text{m}^{-3}$	u / $\text{m}\cdot\text{s}^{-1}$	Φv / $\text{cm}^3\cdot\text{mol}^{-1}$
				SDS + Nonan-1-ol					
	298.15 K			303.15 K			308.15 K		
0.000	1.000966	1498.0	-	0.999555	1509.5	-	0.997734	1519.1	-
0.004	1.000850	1497.9	173.72	0.999435	1509.3	175.13	0.997610	1518.9	176.54
0.008	1.000729	1497.8	173.80	0.999309	1509.2	175.14	0.997480	1518.7	176.52
0.011	1.000655	1497.8	173.82	0.999232	1509.1	175.16	0.997400	1518.5	176.59
0.014	1.000560	1497.7	173.84	0.999133	1508.9	175.22	0.997298	1518.3	176.63
0.016	1.000486	1497.7	173.86	0.999056	1508.8	175.23	0.997219	1518.2	176.61
0.020	1.000370	1497.6	173.88	0.998936	1508.7	175.25	0.997095	1517.9	176.63
0.025	1.000227	1497.5	173.92	0.998788	1508.5	175.28	0.996942	1517.6	176.67
				SDS + Decan-1-ol					
0.000	1.000966	1498.0	-	0.999555	1509.5	-	0.997734	1519.1	-
0.002	1.000896	1497.9	191.41	0.999482	1509.4	193.16	0.997658	1519.0	195.01
0.009	1.000676	1497.7	191.52	0.999252	1509.2	193.27	0.997419	1518.7	195.07
0.011	1.000606	1497.7	191.53	0.999179	1509.1	193.27	0.997343	1518.6	195.08
0.013	1.000533	1497.6	191.54	0.999102	1509.0	193.32	0.997263	1518.4	195.13
0.016	1.000429	1497.5	191.56	0.998994	1508.8	193.34	0.997150	1518.3	195.19
0.020	1.000306	1497.3	191.59	0.998864	1508.6	193.42	0.997016	1518.0	195.21
0.022	1.000239	1497.3	191.60	0.998794	1508.5	193.44	0.996942	1517.9	195.29

Table 5. Partial Molar Volume, $\Phi^{\circ}v$, for Aqueous Surfactants Alcohol Solutions

parameter	298.15 K	303.15 K	308.15K
	SDS ($0.1\ \text{mol}\cdot\text{kg}^{-1}$) + Heptan-1-ol		
$\Phi^{\circ}v/\text{cm}^3\cdot\text{mol}^{-1}$	138.60 ± 0.01^{a} $(139.5)^{b}$	139.39 ± 0.01	139.99 ± 0.01
	SDBS ($0.1\ \text{mol}\cdot\text{kg}^{-1}$) + Heptan-1-ol		
$\Phi^{\circ}v/\text{cm}^3\cdot\text{mol}^{-1}$	138.01 ± 0.006	138.79 ± 0.02	139.66 ± 0.02
	SDS ($0.05\ \text{mol}\cdot\text{kg}^{-1}$) + Octan-1-ol		
$\Phi^{\circ}v\ /\text{cm}^3\cdot\text{mol}^{-1}$	$156.38 \pm 0.003(157.5)^{b}$	157.39 ± 0.006	159.08 ± 0.02
	SDS ($0.1\ \text{mol}\cdot\text{kg}^{-1}$) + Octan-1-ol		
$\Phi^{\circ}v/\text{cm}^3\cdot\text{mol}^{-1}$	156.40 ± 0.02 $(157.5)^{b}$	157.40 ± 0.01	158.92 ± 0.03
	SDS ($0.1\ \text{mol}\cdot\text{kg}^{-1}$) + Nonan-1-ol		
$\Phi^{\circ}v/\text{cm}^3\cdot\text{mol}^{-1}$	$173.71 \pm 0.01(174.7)^{b}$	175.10 ± 0.01	176.51 ± 0.02
	SDS ($0.1\ \text{mol}\cdot\text{kg}^{-1}$) + Decan-1-ol		
$\Phi^{\circ}v/\text{cm}^3\cdot\text{mol}^{-1}$	191.42 ± 0.01 $(191.7)^{b}$	193.13 ± 0.12	194.96 ± 0.02

[a] Standard deviations. [b] Data taken from ref 3.

The partial molar volume of a solute $\Phi^{\circ}v$ reflects the true volume of the solute and the volume change arising from the solute–solvent interactions. It means that the change in $\Phi^{\circ}v$ at different surfactant concentration and temperature should reflect the changes occurring in its environment in the micellar system. The parameter S_v provides information regarding solute–solute interactions. The derived values of the parameter $\Phi^{\circ}v$ as a function of surfactant concentration and temperature are reported in Table 5.

The isentropic compressibility, κ_s, of the solution can be obtained by the Newton–Laplace equation:

$$\kappa_s = 1/u^2\rho \tag{3}$$

The expanded uncertainty of the isentropic compressibility is $\pm\ 6.0\cdot10^{-12}\ \text{Pa}^{-1}$.

Further, the critical micelle concentration (cmc) of SDS in octan-1-ol was determined as the intersection of two straight-line portions of the specific conductance versus SDS concentration plots. The experimentally determined cmc values for SDS in the aqueous-rich region of octan-1-ol at temperatures (298.15, 303.15, 308.15, and 313.15) K, expressed in mole fraction unit, are presented in Table 6 as x_{cmc}.

A clear understanding of the process of micellization is necessary for the explanation of the effects of structural and environmental factors on the value of the cmc and for predicting the effects on it of new structural and environmental variations. The determination of thermodynamic parameters of micellization, $\Delta H^{\circ}_{\text{m}}$, $\Delta G^{\circ}_{\text{m}}$, and $\Delta S^{\circ}_{\text{m}}$ has played an important role in developing such an understanding. From the variation of cmc with temperature, the thermodynamic parameters of micellization can be obtained.

The free energy of micellization, ($\Delta G^{\circ}_{\text{m}}$), may be calculated by choosing for the standard initial state of the nonmicellar surfactant species, which is supposed to be a hypothetical state at unit mole fraction, but with the individual ions or molecules behaving as at infinite dilution, and for the standard final state, which is a micelle itself. The free energy of micellization ($\Delta G^{\circ}_{\text{m}}$) is given by the expression

$$\Delta G^{\circ}_{\text{m}} = RT \ln x_{\text{cmc}} \tag{4}$$

where R is the gas constant and T is absolute temperature. x_{cmc} is a ratio of the molar concentration of the surfactant in the liquid phase at the cmc and that of the solvent in the liquid phase. However, since the number of counterions bound by the micelle, that is, α, usually varies with temperature, this method of calculating

Table 6. Critical Micelle Concentration, x_{cmc}, of Aqueous SDS in the Presence of Octan-1-ol at Different Temperatures and Corresponding Thermodynamic Parameters at 298.15 K

					298.15 K		
M	$x_{\mathrm{cmc}} \cdot 10^4$				$\Delta G^{\circ}{}_{\mathrm{m}}$	$\Delta H^{\circ}{}_{\mathrm{m}}$	$\Delta S^{\circ}{}_{\mathrm{m}}$
$\mathrm{mol \cdot dm^{-3}}$	298.15 K	303.15 K	308.15 K	313.15 K	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{J(mol \cdot K)^{-1}}$
0	1.47	1.52	1.57	1.62	−21.9	−5.0	56.5
0.0010	1.07	1.10	1.12	1.13	−22.66	−4.1	62.1
0.0075	1.07	1.09	1.12	1.13	−22.66	−2.8	66.7
0.0100	1.05	1.07	1.11	1.12	−22.70	−2.2	68.6
0.0180	1.05	1.06	1.10	1.12	−22.71	−1.4	71.4
0.0225	1.02	1.03	1.08	1.10	−22.78	−1.4	71.5
0.0305	1.01	1.02	1.06	1.08	−22.81	−1.5	71.6
0.0360	1.00	1.01	1.05	1.06	−22.83	−1.5	71.6

$\Delta H^{\circ}_{\mathrm{m}}$ and $\Delta S^{\circ}_{\mathrm{m}}$ may be used for ionic surfactants only when the plot of $(1 + \alpha) \log x_{\mathrm{cmc}}$ versus $1/T$ is linear.

The enthalpy of micellization $(\Delta H^{\circ}_{\mathrm{m}})$ can be determined as follows:

$$\Delta H^{\circ}_{\mathrm{m}} = -RT^2 \mathrm{d}[\ln x_{\mathrm{cmc}}]/\mathrm{d}t \qquad (5)$$

and the entropy of micellization $(\Delta S^{\circ}_{\mathrm{m}})$ is obtained from the equation,[23]

$$\Delta G^{\circ}_{\mathrm{m}} = \Delta H^{\circ}_{\mathrm{m}} - T\Delta S^{\circ}_{\mathrm{m}} \qquad (6)$$

The thermodynamic parameters derived from eqs 4 to 6 at 298.15 K for SDS in the presence of octan-1-ol are summarized in Table 6.

The Φv values of heptan-1-ol, octan-1-ol, nonan-1-ol, and decan-1-ol in an aqueous micelle solution of SDS/SDBS at different molalities and temperatures show that a considerable variation occurs in this property for the studied alcohols and depends upon the concentrations of the surfactant and alcohols as well as the temperature. The variations of Φv with molality of heptan-1-ol with surfactants SDS/SDBS at different temperatures show linear behavior, whereas in the case of octan-1-ol, at (0.05 and 0.10) $\mathrm{mol \cdot kg^{-1}}$ of aqueous SDS, it shows a nonlinear trend with the molal concentration of alcohol and that Φv is very much dependent upon the molalities of surfactant and alcohol as well as the temperature. The nonlinear behavior of Φv suggests that the shapes and size of the micelles are changing due to the presence of the octan-1-ol or maybe the alcohol molecules are changing locations in the micellar aggregates.[14] In the case of solutions containing nonan-1-ol/decan-1-ol the variations of Φv with alcohol concentration are linear at very low concentrations of alcohols.

The partial molar volume of a solute, $\Phi^{\circ} v$, reflects the volume change arising from the solute−solvent interaction. The change in $\Phi^{\circ} v$ at different surfactant concentrations and temperatures should reflect the changes occurring in its environment in the micelle system. A perusal of Table 5 reveals that the values of $\Phi^{\circ} v$ are positive, and they increase with the rise in temperature for the studied alcohols in aqueous surfactant solutions, suggesting strong solute−solvent interactions. It was shown[24] that the $\Phi^{\circ} v$ dependence of the surfactant concentration is the result of two contributions: the alcohol distribution between the two phases, that is, the aqueous and the micellar phase, and the chemical displacement of the micellization equilibrium due to the added alcohol. The latter contribution tends to predominate the longer the alcohol alkyl chain. The value of $\Phi^{\circ} v$ for heptan-1-ol at 0.10 $\mathrm{mol \cdot kg^{-1}}$ aqueous SDS/SDBS solutions shows that there is a significant difference between $\Phi^{\circ} v$ for alcohol and in aqueous data, indicating that the alcohol molecules are partly solubilized in the micelle solution of surfactants. The partial molar volumes of the alcohols in the micellar state are found to be additive with a $\mathrm{CH_2}$-group contribution of 17.1 $\mathrm{cm^3 \cdot mol^{-1}}$ in nonaqueous solvents.[25] The partial apparent molar properties of transfer provide qualitative as well as quantitative information regarding solute−cosolvent interactions without taking into account the effects of solute−solute interactions.[6]

The plots of κ_s of aqueous micelle solutions in the presence of all of the studied alcohols show an increasing trend at studied temperatures and are given in the Supporting Information. The increase in the compressibility may arise because of the decrease in the structured water as a result of transfer of the additive alcohols from the aqueous phase to the micelle aggregates.[10] This change may be compensated by the loss of free space in the micelle interior upon the addition of alcohols. It results in an increase in the compressibility of the micellar solutions. According to Gonzalez-Perez et al.,[26] hydration makes a negative contribution to the compressibility of a solute, as observed for monomeric surfactants as well as for simple electrolytes or their ions. According to Hoiland et al.,[25] a plot of density or compressibility versus alcohol concentration in aqueous SDS−hexan-1-ol solutions was found to be significantly curved at low alcohol concentrations, typically below 0.04 $\mathrm{mol \cdot kg^{-1}}$. The pronounced curvature at low alcohol concentrations is mainly an effect of the changes in cmc. However, above this molal concentration, a region of almost linear relationship is observed. A similar observation is found in the present study also.

A close look at Table 6 reveals that there is a small difference in x_{cmc} of SDS due to the presence of octan-1-ol. The cmc lowering of the surfactants by the small addition of alcohols may be due to their direct action on water structure and the subsequent addition may cause secondary effects such as their solubilization in micelle and decrease of hydrophobic effect.[8] A close perusal of Table 6 indicates that, in the case of the studied alcohol, the decrease in cmc occurs steeply over a narrow composition range, M = (0.0 to 0.036) $\mathrm{mol \cdot dm^{-3}}$. The values of cmc increase with an increase in temperature from (298.15 to 303.15) K. The magnitude of cmc values in presence of alcohols are relatively smaller and suggest the solubilization of these additives in the hydrocarbon environment of the micelles. According to the literature,[2] the hydrocarbon chain of the alcohol should penetrate the micellar

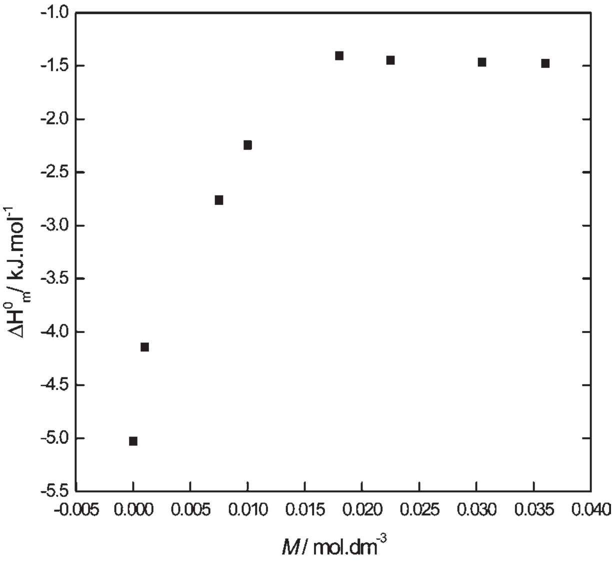

Figure 1. Dependence of enthalpy of micellization, $\Delta H^\circ{}_m$, of SDS as a function of added octan-1-ol at 298.15 K.

Table 7. Chemical Shift (δ) of Protons Close to the Tail of SDS in the Presence and in the Absence of Monohydric Alcohols in SDS (0.10 mol·kg^{-1}) at T = 295 K

alcohol	proton peaks in SDS micellar solutions/ppm	
mol·kg^{-1}	peak c	peak d
0.0	1.612	3.949
Heptan-1-ol		
0.0184	1.577	3.916
0.0438	1.581	3.919
0.0684	1.583	3.919
Octan-1-ol		
0.0087	1.627	3.973
0.0147	1.629	3.971
0.0476	1.630	3.965
Nonan-1-ol		
0.0050	1.596	3.941
0.0080	1.634	3.998
0.0132	1.658	3.998
Decan-1-ol		
0.0060	1.593	3.938
0.0126	1.642	3.985
0.0275	1.644	3.984

interior, while the polar head groups should remain at the micellar surface. The alcohol polar groups, present at the micellar surface, would lead to a reduction in the effect due to the repulsion of the surfactant head groups. According to the pseudo phase model for micellization,[27] octan-1-ol is considered as a nonionic surfactant the cmc of which is equal to its water solubility (0.0038 mol·dm^{-3}). The cmc of SDS is 0.008 mol·dm^{-3}. Moya et al.[5] studied the aqueous SDS–octan-1-ol system considering the alcohol as a nonionic surfactant. In a typical specific conductivity versus total concentration plot they obtain two break points which correspond to two different aggregation steps. This was due to the octan-1-ol which acted as a highly surface active impurity in SDS. They concluded that the true cmc value is that of the lower concentration transition giving isometric (spherical or ellipsoidal), almost fully ionized micelles. The higher concentration transition corresponds to the transition to anisometric (probably rod-like) micelles, accompanied by the micellization of counterion.

The standard Gibbs free energy of micellization, ΔG°m, enthalpy of micellization, ΔH°_m, and entropy of micellization, ΔS°_m, has been used to obtain information on the solubilization site of the additives in the micelle. The thermodynamic parameters obtained in this study provide quantitative evidence for the relative ease of transfer of octan-1-ol from the aqueous to the micellar phase. From Table 6, it is evident that in all cases ΔG°_m is negative and its magnitude remains practically constant over the entire alcohol composition range, indicating that it is solubilized preferentially in the micellar aggregates. An increase in the magnitude of ΔG°_m with temperature has been reported in the literature[10] which indicates that the hydrophobic effect increases in magnitude with increasing temperature which, in turn shows that penetration of these solubilizates into the micelle becomes more favorable at higher temperature.

The ΔH°_m data show that the process of solubilization of octan-1-ol in aqueous micelle solutions of SDS is exothermic. The negative values of ΔH°_m indicate that strong interactions are occurring between octan-1-ol and the micellar system and that these interactions are greatest at the lowest alcohol concentration, 0.0010 mol·dm^{-3}. This suggests that, at very low concentrations, octan-1-ol solubilized in SDS is located near the outer surface of the micelle where the negatively charged headgroup of the surfactant and the polar group of the alcohol can interact, presumably by dipole–dipole or ion–dipole interactions. On increasing the concentration of octan-1-ol, the negative magnitude of ΔH°_m decreases regularly, as reported in Figure 1, suggesting that, at higher concentrations, octan-1-ol is solubilized in the palisade layer of the micelle. ΔS°_m values are positive and shows an increasing trend with the increase in concentration of octan-1-ol. The positive entropy change indicates that in the system studied the entropy is dominating over the micellization process. This observation may be explained as due to the reorganization of water molecules at the micellar solubilization of alcohol. Such an effect would indeed cause a smaller decrease in entropy and enthalpy, which is in agreement with the observed values of ΔH°_m and ΔS°_m. The positive ΔS°_m values are attributed to the disruption of water structure around the hydrocarbon part of these additive molecules as they transfer from the aqueous bulk phase to nonaqueous part of the micellar aggregates. At the same time, water–water bonds are broken, which in turn increase the randomness of the hydrocarbon chains in the micellar core.[28] Thus, the decrease in cmc on addition of an additive may be seen in terms of establishment of additional hydrophobic interactions between the hydrophobic part of the surfactant and additive molecules. In light of the above discussion, it may be concluded that octan-1-ol behaves as a penetrating additive. The results obtained from the present investigation are similar to those in case of aqueous SDS and monohydric medium chain alcohols (C_3–C_6) reported previously.[8] The enthalpy and entropy changes are associated with the effects of alcohol additives on micellization of SDS molecules, which consist of hydrophobic contributions. It can be seen that $\Delta G^\circ_m < 0$ is weakly dependent on alcohol concentration in aqueous surfactant solutions. This behavior reasonably accounts for the observed compensation between ΔH°_m and ΔS°_m values, leaving ΔG°_m unaffected.

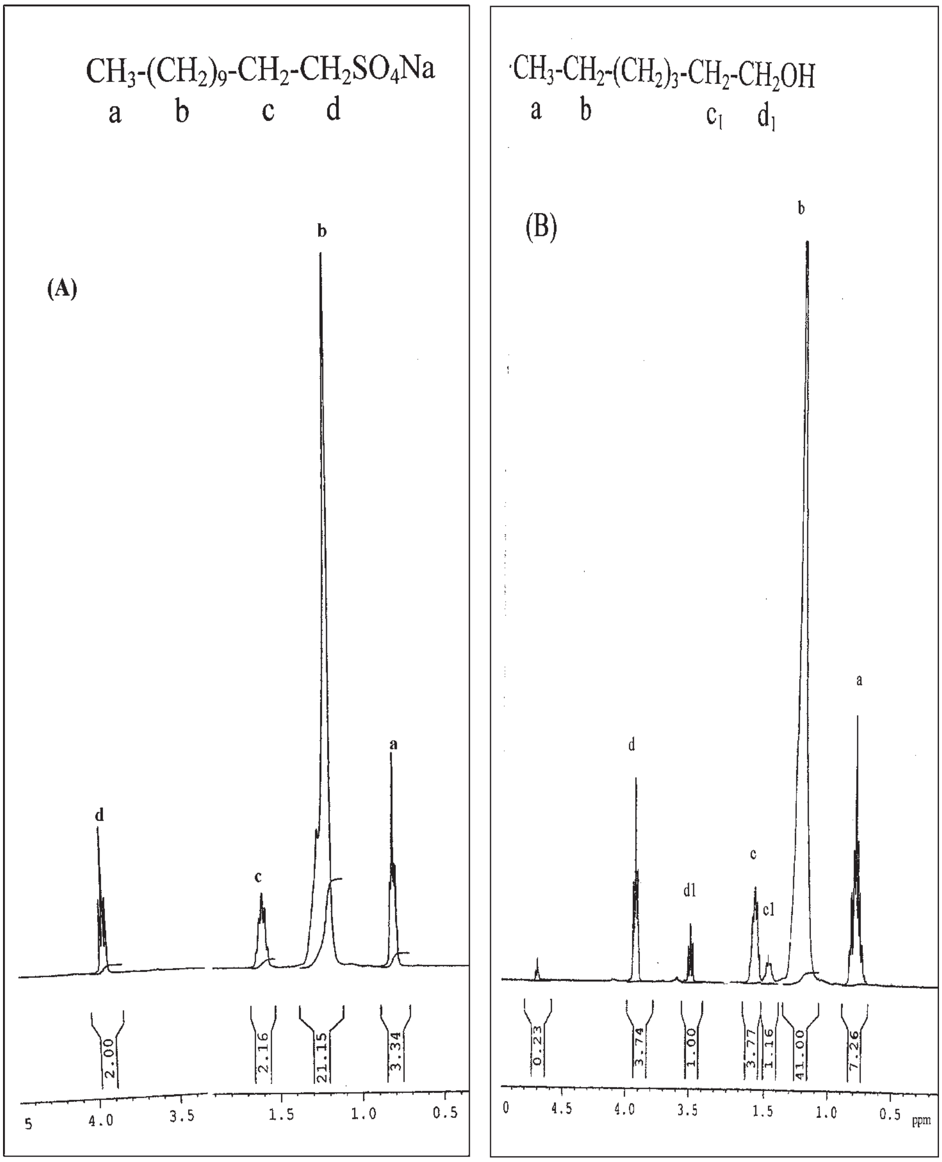

Figure 2. ^{1}H NMR spectra in ppm at 295 K: (A) 0.1 mol·kg^{-1} SDS; (B) 0.0184 mol·kg^{-1} heptan-1-ol in 0.1 mol·kg^{-1} SDS in D_2O.

The site of solubilization may be located using ^{1}H NMR studies.[6,14,29] The ^{1}H NMR chemical shift studies of solutions containing 0.10 mol·kg^{-1} SDS and different concentrations of alcohols are reported in Table 7. Typical spectra for 0.10 mol·kg^{-1} aqueous SDS and the assignment of various peaks are given in Figure 2A, whereas that in the presence of heptan-1-ol (0.0184 mol·kg^{-1}) is presented in Figure 2B. A careful inspection of various ^{1}H signals in the case of pure surfactant solution and a shift in the position of these signals upon mixing various alcohols helps to deduce the preferential solubilization sites of studied alcohols in aqueous SDS solution. A comparison of the chemical shift (δ) of the proton spectra of aqueous SDS solutions, with those containing studied alcohols clearly indicates that the site for preferential solubilization of alcohol is close to the headgroup of micelle. This is apparent from the significant change in frequencies of the proton peaks (peaks c and d) of Table 7. In SDS solutions, at the studied concentration (0.10 mol·kg^{-1}), peaks c and d show a small but downfield shift with an increase in the concentration of alcohols under consideration.

The peaks for the proton close to the tail of SDS are overlapping with the peaks due to methylene protons of alcohols. This is the reason that it is difficult to interpret the shift in the position of protons close to the tail of SDS of NMR spectra. Apart from this, the presence of a large number of protons, (close to the tail of SDS) appearing over a narrow range of chemical shift, makes their exact assignment unrealistic. Since the change of chemical shift caused by the aggregation of molecules is usually related to structural changes,[6] the NMR experiments imply that the location of the added alcohols is in the interfacial region of a micellar aggregates.

The ^{13}C chemical shift studies of surfactants in the presence of various additives are reported in literature.[30−33] A careful analysis of various ^{13}C signals, in the case of aqueous SDS, and a shift in the position of these signals upon adding various alcohols will help us to deduce the preferred solubilization sites of added alcohols in the aqueous surfactant solutions. In the present case, the ^{13}C chemical shift studies of a 0.1 molkg^{-1} SDS solution were obtained in the absence and in the presence of octan-1-ol, nonan-1-ol, and decan-1-ol and the variations of the chemical shifts (ppm)

Table 8. Difference of ^{13}C Chemical Shifts between SDS and SDS + Alcohols for Each Reported Peak with $\Delta\delta$/ppm = $\delta_{SDS} - \delta_{SDS+alcohol}$

alcohol	C1	C2	C3	C10	C11	C12
SDS	0	0	0	0	0	0
			SDS + Octan-1-ol			
0.0087	−0.03	−0.1	−0.05	−0.02	−0.02	−0.07
0.0147	0.02	−0.13	−0.14	−0.03	−0.03	−0.06
0.0476	0.53	0.29	0.33	0.42	0.44	0.45
			SDS + Nonan-1-ol			
0.008	−0.01	−0.09	−0.05	−0.02	−0.02	−0.06
0.0132	0.01	−0.12	−0.13	−0.1	−0.05	−0.05
0.0312	0.09	−0.16	−0.19	−0.13	−0.04	−0.02
			SDS + Decan-1-ol			
0.006	0.02	−0.02	0.02	−0.02	−0.01	0.02
0.0126	0.03	−0.11	−0.15	−0.13	−0.07	0.02
0.0275	0.06	−0.11	−0.22	−0.2	−0.1	−0.02

of the different carbon atoms of micellized SDS molecules are reported in Table 8a (given in the Supporting Information). The difference of ^{13}C chemical shifts between SDS and SDS + alcohols for each reported peak is presented in Table 8.

Figure 3a−c represents a variation in the chemical shifts of carbons close to the headgroup of the surfactant (i.e., C_1, C_2 and C_3) with respect to an increase in the amount of alcohols added. A qualitative comparison among C_1, C_2, and C_3 suggests that C_1 carbon undergoes a maximum upfield shift with an increase in the concentration of added alcohols for all the SDS + alcohol systems which suggests that they experience shielding effects as soon as they realize the presence of additive, that is, alcohol molecules in their vicinity.[31] It suggests that the solubilization site for the added alcohols in the surfactant may be near to C_1. Both C_2 and C_3 carbons experience downfield shift for the studied alcohols for all of the concentrations except in the case of SDS containing octan-1-ol, where at higher concentrations (>0.008 mol·kg^{-1}) of the alcohol an upfield shift of the carbons has been seen. The trend observed in carbon chemical shifts may be attributed to the chain length of the added alcohols due to the strong ion−dipole interaction between the negatively charged SDS headgroup and the hydroxyl group of the alcohol. From the volumetric data also it was suggested that the shapes and size of the micelles are changing due to the presence of the octan-1-ol or maybe the alcohol molecules are changing locations in the micellar aggregates, whereas in the case of solutions containing nonan-1-ol/decan-1-ol no such trend was seen. Reekmans et al.[30] studied the effect of long chain alcohols on aggregation behavior of ionic surfactants usingthe fluorescence quenching process. They concluded that for alcohols the chain length is the apparently the factor determining the effects on the aggregation number of the surfactant. The alcohols under present study are believed to conserve or increase the size of the micelle aggregates. The effect becomes stronger for an alcohol with a longer chain.

The hydrocarbon tail carbons (C_{10}, C_{11}, and C_{12}) of SDS in the presence of added alcohols undergo a downfield shift at low concentration and show an upfield shift at high concentration in the case of octan-1-ol as an additive. However, in the case of nonan-1-ol/decan-1ol C_{10} and C_{11} carbons exhibit a downfield shift, whereas in C_{12} carbon no definite trend in chemical shift is seen. The results of the present study agree well with those reported in ^{1}H NMR spectra of SDS molecules in the presence of studied alcohols which concludes that the site for preferential solubilization site of alcohol is close to the headgroup of micelle. The chemical shifts of carbon atoms are associated with the effects of

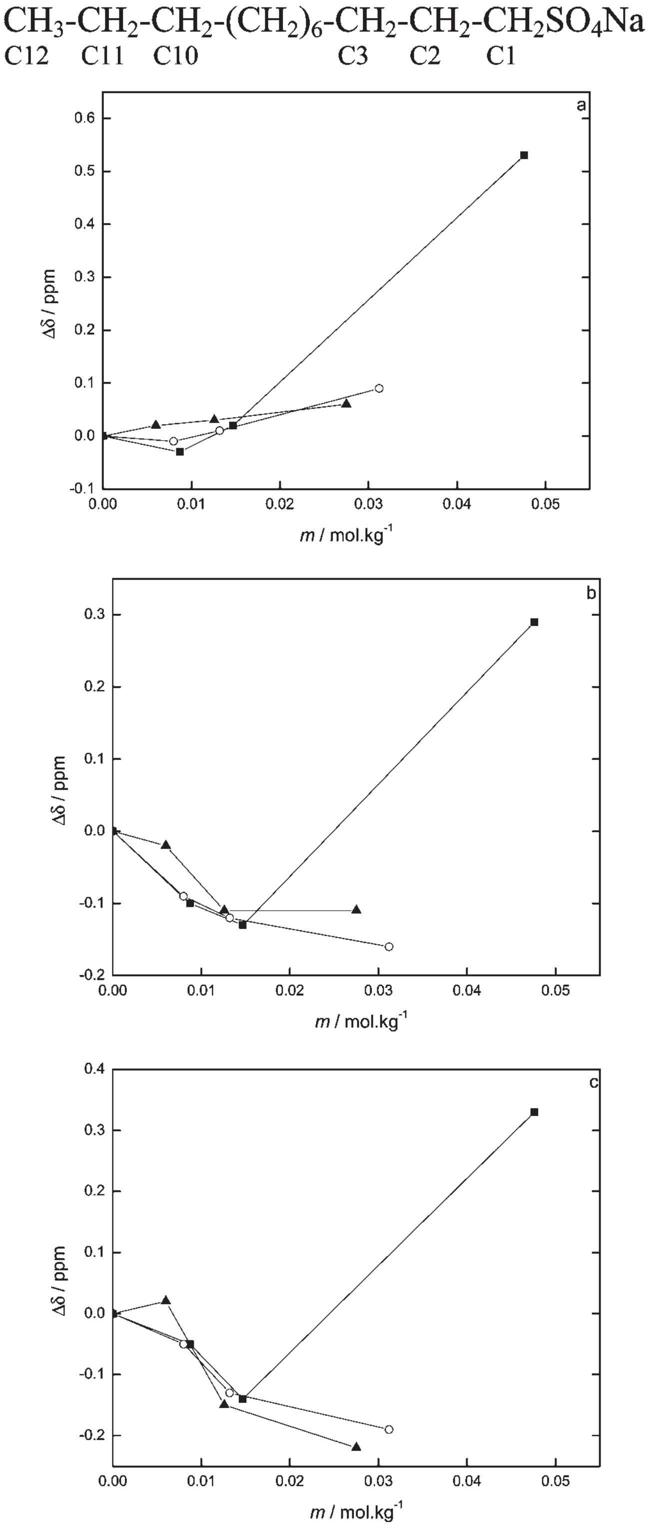

Figure 3. Difference of ^{13}C chemical shifts between SDS and SDS + alcohols: ■, SDS + octan-1-ol; ○, SDS + nonan-1-ol; and ▲, SDS + decan-1-ol (a) C_1 carbon, (b) C_2 carbon, and (c) C_3 carbon.

alcohol additives on micellization of SDS molecules which consist of hydrophobic contributions. The chemical shift shows a decrease as the hydrocarbon chain length of alcohols becomes larger.

CONCLUSION

The thermodynamic investigations for aqueous SDS/SDBS micellar solutions at different concentrations containing alcohols clearly indicate the strong alcohol−aqueous surfactant interactions as concluded from the studied partial molar property. The decrease in cmc on the addition of an additive should be seen in terms of the establishment of additional hydrophobic interactions between the hydrophobic part of the surfactant and additive molecules. The micellization process is governed primarily by the entropy increase and the driving force for micellization is mainly entropic, that is, the tendency of the hydrophobic group of the surfactant to transfer from the solvent to the interior of the micelle. The site for preferential solubilization of alcohol is close to the headgroup of micelle as interpreted from ^{1}H and ^{13}C NMR studies. The result of this analysis thus shows the effect of chain length of alcohols on micellization of SDS molecules. The chemical shifts of carbon atoms are associated with the effects of alcohol additives on the micellization of SDS molecules which consist of hydrophobic contributions. The more hydrophobic alcohols are, the more marked decrease in chemical shift of carbon atom close to the headgroup of the surfactant is observed.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental data of specific conductance of aqueous SDS as well as that in the presence of octan-1-ol. Plots of isentropic compressibility, k_s, of aqueous solutions of SDS with various alcohols at different temperatures. ^{13}C studies of SDS in the presence and in the absence of monohydric alcohols (Table 8a). This material is available free of charge via the Internet at http://pubs.acs.org.

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