Thermodynamic and Interfacial Adsorption Studies on the Micellar Solutions of Alkyltrimethylammonium Bromides in Ethylene Glycol (1) + Water (2) Mixed Solvent Media†

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Micellization behavior of three alkyltrimethylammonium bromides, viz., hexadecyl-, tetradecyl-, and dodecyltrimethylammonium bromide (CTAB, TTAB, and DTAB, respectively) in ethylene glycol (EG) (1) + water (2) mixed solvent media with varying mass fractions of EG (w_1) has been studied by means of electrical conductivity and surface tension measurements. Temperature dependence of the critical micelle concentrations was also investigated to understand the micellar thermodynamics of these systems. The mass action model of micelle formation was applied to obtain the thermodynamic parameters of micellization. Only small differences have been observed in the standard molar Gibbs energies of micellization over the temperature range investigated. The enthalpy of micellization was found to be negative in all cases, whereas the entropic contributions were always positive, indicating that an enthalpy−entropy compensation effect is the governing factor for micellization. Surface tension measurements also provide information about the effects of the addition of ethylene glycol to water on the excess surface concentration, minimum area per surfactant molecule, the surface pressure at the critical micelle concentrations, and standard Gibbs energy of adsorption. The Gordon parameters for the EG (1) + water (2) mixtures were also estimated by means of surface tension measurements to assess the ability of EG (1) + water (2) mixtures to bring about the self-association of the surfactants investigated.

Introduction

Surfactants are widely used in both industry and everyday life, and their properties in aqueous solutions have received considerable attention. Recently, the aggregation phenomenon of amphiphiles in nonaqueous media has been the subject of many researchers due to the increasing use of these materials in such areas as lubrication and cleaning operations, which require water-free or water-poor media.[1,2] The solvents used in these studies are strongly polar with water-like properties; some common examples include ethylene glycol, formamide, and glycerol.[3−12] Most of these investigations focused mainly on two aspects: the requirement from a solvent for amphiphilic assembly and the structural properties of the aggregates formed in these media. To address these issues, a frequently used approach is the gradual replacement of water by other polar solvents, as this allows one to explore a wide range of polarities. Several studies have been carried out following this approach.[13−21] For the amphiphilic aggregation to occur, the solvent media should have high cohesive energies, dielectric constants, and considerable hydrogen bonding ability.[22,23]

In the present work, the micellization behavior of three alkyltrimethylammonium bromides, viz., hexadecyltrimethylammonium bromide (CTAB), tetradecyltrimethylammonium bromide (TTAB), and dodecyltrimethylammonium bromide (DTAB) in EG (1) + water (2) mixed solvent media has been studied. Previously, very few studies on these systems have been reported. Backlund et al.[24] investigated the aggregation and phase behavior of TTAB in water, EG, and their mixtures at 30 °C. Ruiz[11] reported the thermodynamic studies of TTAB in EG (1) + water (2) mixtures. Gharibi et al.[25] have also carried out electrochemical studies associated with micellization of TTAB, among other cationic surfactants, in the same solvent mixtures at 25 °C. In this investigation, we have carried out conductivity and surface tension measurements on the systems mentioned above to study their micellization behavior. The influence of temperature on the micellization and adsorption behaviors of these amphiphiles will also be investigated. The ability of EG (1) + water (2) mixtures to bring about self-association will be characterized by the Gordon parameter.[26]

Experimental

The surfactant CTAB was purchased from Sigma. TTAB and DTAB were of Fluka (Switzerland) purum grade, and these were used as received. Ethylene glycol (99 % +, spectroscopic grade) was from Aldrich. Doubly distilled water (specific conductance, (2 to 3) $\mu S \cdot cm^{-1}$) was used to prepare the solutions. All experiments were carried out with freshly prepared solutions.

The conductometric measurements were carried out on a Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip-type cell of cell constant 1.14 cm^{-1}. The cell was calibrated by the method of Lind et al.[27] using aqueous potassium chloride solutions. Solutions were prepared by mass for conductance runs, the molalities being converted to molarities by the use of densities measured with an Ostwald−Sprengel type pycnometer of about 25 cm^3 capacity. The experimental uncertainties in density measurements were always within 0.01 %. Corrections were made for the specific conductance of solvents at all temperatures. The measurements were made in a water bath maintained within ± 0.01 K of the desired temperature.

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† Part of the special issue “Robin H. Stokes Festschrift”.

10.1021/je8005024 CCC: $40.75 © 2009 American Chemical Society
Published on Web 12/04/2008

The surface tensions of the surfactant solutions were measured with a Krüss (Germany) K9 tensiometer by the platinum ring detachment method. The tensiometer was connected to a water-flow cryostat to maintain the temperature equilibration. Prior to each measurement, the ring was heated briefly by holding it above a Bunsen burner until glowing. Several independent solutions were prepared by mass, and duplicate measurements were performed to check the reproducibility. The uncertainty of the measurements was within $\pm\, 1 \cdot 10^{-3}\ \mathrm{N \cdot m^{-1}}$.

Results and Discussion

The conductivities (κ) of CTAB, TTAB, and DTAB in EG (1) + water (2) mixtures containing (0.00, 0.10, 0.20, 0.30, 0.40, and 0.50) mass fractions of EG (w_1) at 298.15 K are given in Table 1, whereas Table 2 lists the conductivities of these surfactants in EG (1) + water (2) mixture with $w_1 = 0.30$ at (303.15, 308.15, 313.15, 318.15, and 323.15) K. The critical micellar concentrations (cmc) were determined from the inflections in the plots of conductivity as a function of the surfactant concentration (C). The data points above and below the inflection are fitted to two linear equations, and the cmc was obtained from the intersection. This method is found to be reliable and convenient for the present system because of the significant variations of conductivity with surfactant concentration in the pre- and postmicellar regions which allowed us to draw two unambiguous straight lines above and below the cmc. The ratio of the slopes of the plots of κ versus C above and below the cmc gives an estimate of the micellar degree of counterion dissociation (α). A representative plot (Figure 1) shows the concentration dependence of the conductivity of TTAB in EG (1) + water (2) mixtures with varying amounts of EG. Figure 2, on the other hand, shows the concentration dependence of the conductivity of CTAB in a given EG (1) + water (2) mixture with $w_1 = 0.30$ at different temperatures. Table 3 lists the values of cmc and the micellar degree of counterion dissociation (α) of the surfactants in different EG (1) + water (2) media at 298.15 K. Table 4 reports the cmc and α values in the mixture with $w_1 = 0.30$ in the temperature range (303.15 to 323.15) K. The cmc values of these surfactants in water were found to be in good agreement with those previously reported in the literature.[28] The micellar degrees of counterion dissociation for a given surfactant are found to increase as the mixed solvent media get richer in EG (cf. Table 3). An increase in cmc originates mainly from the small magnitude of the tail transfer free energy from EG compared to that from water. This effect can be quantified in the EG (1) + water (2) micellar solutions investigated through the estimation of free energy for the transfer of one methylene CH_2 group from the bulk phase to the micellar pseudophase ($\Delta G^0_{CH_2}$) by using eq 1[6,28]

$$(2-\alpha)\ln \mathrm{cmc} = \mathrm{const} + m\left[\frac{\Delta G^0_{CH_2}}{RT}\right] \tag{1}$$

According to this equation, $\Delta G^0_{CH_2}$ can be estimated from the slope of the linear plot of $(2-\alpha)\ln$ cmc against the number of carbon atoms (m) in the surfactant chain for a homologous series of surfactants. Good straight lines were obtained for pure water and for the five EG (1) + water (2) mixtures studied. Table 5 summarizes the $\Delta G^0_{CH_2}$ values thus obtained. The values reported here in water are found to be in good agreement with those reported in the literature.[6,28]

From Tables 3 and 4, it is apparent that the degrees of counterion dissociation for the surfactants increase regularly with both EG addition and temperature increase. This observed increase in α may be attributed to a decrease in the charge density on the micellar surface caused by the decrease in the aggregation number of the micelle.

The ability of EG (1) + water (2) mixtures to bring about the self-association of the amphiphiles can be related to the cohesive energy density,[29] which can be conveniently characterized by the Gordon parameter, $G = \gamma/V^{1/3}$, where γ and V are, respectively, the solvent surface tension and molar volume. Table 6 shows the Gordon parameter values for the different mixtures used as a bulk phase in the micellar solutions studied. The G parameter points out that an increase in the amount of EG in EG (1) + water (2) mixtures results in a decrease in the solvent cohesiveness, thereby improving the solvation of the hydrocarbon tails in the bulk phase and decreasing the solvophobic effect. The increase in the solubility of the hydrocarbon tails in EG (1) + water (2) mixtures gives rise to an increase in the cmc as noted in Table 3.

To analyze the variation of cmc with temperatures, we have considered the mass-action model for micellization. According to this model, the process of micellization of cationic surfactants may be described by

$$n\mathrm{D}^+ + (n-p)\mathrm{X}^- \leftrightarrow \mathrm{M}^{p^+} \tag{2}$$

where D^+ represents the surfactant ions, X^- the corresponding counterions, and M^{p+} the aggregate of n monomers with an effective charge of p. The Gibbs energy of micelle formation per mole of surfactant, ΔG^0_{m}, is given by

$$\Delta G^0_{\mathrm{m}} = RT\left[-\frac{1}{n}\ln a_{\mathrm{M}^{p+}} + \ln a_{\mathrm{D}^+} + \left(\frac{p}{n}\right)\ln a_{\mathrm{X}^-}\right] \tag{3}$$

in which a represents the activity of the species indicated. If the aggregation number (n) is large, the first term in the parenthesis is negligibly small, and both a_{D^+} and a_{X^-} can be replaced by the corresponding activities at the cmc. In addition, taking into account that cmc's occur in dilute solutions, the activity can again be replaced by the concentration of surfactant (expressed in mole fractions) at the cmc. Introduction of these approximations in eq 3 yields[30]

$$\Delta G^0_{\mathrm{m}} = (2-\alpha)RT\ln x_{\mathrm{cmc}} \tag{4}$$

where $\alpha = p/n$ is the degree of counterion dissociation and x_{cmc} is the cmc of a surfactant in mole fraction unit. The corresponding enthalpy change (ΔH^0_{m}) is given by

$$\Delta H^0_{\mathrm{m}} = -RT^2\left[(2-\alpha)\left(\frac{\partial \ln x_{\mathrm{cmc}}}{\partial T}\right)_p - \ln x_{\mathrm{cmc}}\left(\frac{\partial \beta}{\partial T}\right)_p\right] \tag{5}$$

If the change in α with temperature is small over the temperature range investigated, this equation can be expressed as

$$\Delta H^0_{\mathrm{m}} = -(2-\alpha)RT^2\left(\frac{\partial \ln x_{\mathrm{cmc}}}{\partial T}\right)_p \tag{6}$$

Therefore, the enthalpy of micellization may be obtained if the dependence of the cmc on temperature is known. In the present study, the contribution of the second term (within the parentheses) in eq 5 is negligible, so we used eq 6 to estimate ΔH^0_{m} values. With this purpose, $\ln x_{\mathrm{cmc}}$ values for the three surfactants in the EG (1) + water (2) mixture with $w_1 = 0.30$ were plotted against T, and the slope was taken as equal to $((\partial \ln x_{\mathrm{cmc}})/(\partial T))_p$. These plots are shown in Figure 3. A linear plot was observed for each of the surfactant systems investigated, and this may be ascribed to the linear dependence of the $\ln x_{\mathrm{cmc}}$ values on the disruption of the water structure caused by the presence of the cosolvent molecules in this mixture. A similar kind of linearity has also been observed by Ruiz[11] for

Table 1. Conductivities and Corresponding Molarities of Alkyltrimethylammonium Bromides in EG (1) + Water (2) Mixtures with $w_1 = 0.00$, 0.10, 0.20, 0.30, 0.40, and 0.50 at 298.15 K

$\frac{C}{\mathrm{mol \cdot dm^{-3}}}$	$\frac{\kappa}{\mu\mathrm{S \cdot cm^{-1}}}$	$\frac{C}{\mathrm{mol \cdot dm^{-3}}}$	$\frac{\kappa}{\mu\mathrm{S \cdot cm^{-1}}}$	$\frac{C}{\mathrm{mol \cdot dm^{-3}}}$	$\frac{\kappa}{\mu\mathrm{S \cdot cm^{-1}}}$	$\frac{C}{\mathrm{mol \cdot dm^{-3}}}$	$\frac{\kappa}{\mu\mathrm{S \cdot cm^{-1}}}$	$\frac{C}{\mathrm{mol \cdot dm^{-3}}}$	$\frac{\kappa}{\mu\mathrm{S \cdot cm^{-1}}}$	$\frac{C}{\mathrm{mol \cdot dm^{-3}}}$	$\frac{\kappa}{\mu\mathrm{S \cdot cm^{-1}}}$
		$w_1 = 0.00$						$w_1 = 0.30$			
CTAB		TTAB		DTAB		CTAB		TTAB		DTAB	
0.000162	14.3	0.00044	39.4	0.002039	186.0	0.000239	12.5	0.00074	35.6	0.002311	107.0
0.000313	26.5	0.00085	75.5	0.003951	352.0	0.000464	22.7	0.00143	67.5	0.004479	205.0
0.000456	39.2	0.00124	109.0	0.005747	502.0	0.000676	32.1	0.00208	96.0	0.006518	294.0
0.000590	50.7	0.00160	140.0	0.007437	643.0	0.000875	41.0	0.00270	124.0	0.008439	376.0
0.000717	61.6	0.00194	170.0	0.009030	775.0	0.001064	49.5	0.00328	150.0	0.010252	453.0
0.000836	71.8	0.00227	198.0	0.010536	899.0	0.001242	57.6	0.00383	174.0	0.011965	524.0
0.000949	81.4	0.00258	224.0	0.011959	1000	0.001411	65.0	0.00435	197.0	0.013587	591.0
0.001056	87.6	0.00287	249.0	0.013308	1150	0.001571	72.7	0.00485	219.0	0.015125	653.0
0.001157	90.6	0.00315	273.0	0.014588	1260	0.001724	78.6	0.00532	239.0	0.016584	711.0
0.001254	92.0	0.00341	296.0	0.015803	1320	0.001868	82.3	0.00577	252.0	0.017972	764.0
0.001346	94.0	0.00366	313.0	0.018061	1390	0.002006	84.7	0.00620	263.0	0.019293	816.0
0.001433	96.0	0.00390	323.0	0.020113	1440	0.002138	86.8	0.00661	272.0	0.020552	859.0
0.001516	98.0	0.00413	331.0	0.021987	1480	0.002263	88.5	0.00700	278.0	0.021753	895.0
0.001596	100.0	0.00434	338.0	0.023705	1520	0.002383	90.1	0.00737	284.0	0.022899	923.0
0.001672	102.0	0.00455	343.0	0.025285	1550	0.002498	91.6	0.00772	289.0	0.023996	945.0
0.001745	104.0	0.00475	348.0	0.029349	1640	0.002608	93.0	0.00807	294.0	0.025045	962.0
0.001881	107.0	0.00512	357.0	0.032626	1710	0.002814	96.0	0.00871	302.0	0.026050	975.0
0.002006	110.0	0.00547	365.0			0.003004	98.0	0.00930	310.0	0.027014	987.0
0.002122	112.0	0.00578	371.0			0.003180	100.0	0.00985	316.0	0.028827	1010
0.002229	115.0	0.00608	377.0					0.01036	323.0	0.030501	1030
		0.00635	383.0					0.01174	341.0	0.032053	1050
		0.00661	388.0					0.01313	360.0	0.036153	1110
		0.00685	393.0					0.01454	378.0		
		0.00748	406.0					0.01604	395.0		
		0.00843	426.0								
		0.00949	450.0								
		0.01063	474.0								
		$w_1 = 0.10$						$w_1 = 0.40$			
CTAB		TTAB		DTAB		CTAB		TTAB		DTAB	
0.000188	15.9	0.00066	48.1	0.002241	164.0	0.000310	12.3	0.00079	29.8	0.002345	88.4
0.000365	28.3	0.00128	91.0	0.004344	312.0	0.000601	22.9	0.00153	56.5	0.004548	166.0
0.000531	39.1	0.00187	132.0	0.006322	447.0	0.000875	32.9	0.00223	81.2	0.006622	237.0
0.000687	50.0	0.00242	169.0	0.008185	577.0	0.001133	42.1	0.00289	103.0	0.008576	303.0
0.000835	60.3	0.00294	206.0	0.009943	693.0	0.001378	51.1	0.00351	125.0	0.010423	363.0
0.000974	70.3	0.00343	239.0	0.011605	801.0	0.001609	59.3	0.00410	145.0	0.012169	420.0
0.001106	78.9	0.0039	270.0	0.013178	903.0	0.001828	67.1	0.00466	164.0	0.013824	473.0
0.001231	82.9	0.00434	288.0	0.014669	989.0	0.002036	74.5	0.00519	182.0	0.015394	523.0
0.00135	85.7	0.00476	301.0	0.016085	1110	0.002233	81.3	0.00569	199.0	0.016885	570.0
0.001463	88.0	0.00516	310.0	0.017431	1160	0.002421	87.4	0.00617	214.0	0.018303	615.0
0.001571	90.1	0.00554	318.0	0.018712	1200	0.002600	91.7	0.00662	229.0	0.019654	658.0
0.001673	91.0	0.0059	325.0	0.019933	1230	0.002771	94.0	0.00706	243.0	0.020943	697.0
0.001771	93.0	0.00624	331.0	0.021097	1250	0.002934	96.0	0.00748	254.0	0.022172	734.0
0.001865	95.0	0.00657	337.0	0.022210	1270	0.003090	98.0	0.00787	263.0	0.023347	769.0
0.001954	97.0	0.00689	342.0	0.023273	1290	0.003239	101.0	0.00825	272.0	0.024471	800.0
0.002039	99.0	0.00719	348.0	0.024291	1310	0.003382	102.0	0.00862	280.0	0.025547	829.0
0.002200	102.0	0.00776	357.0	0.026200	1340	0.003650	106.0	0.0093	292.0	0.027567	878.0
0.002347	105.0	0.00828	366.0	0.027958	1370	0.003897	108.0	0.00993	301.0	0.029429	916.0
0.002733	113.0	0.00876	374.0	0.032554	1460	0.004126	111.0	0.01051	309.0	0.031150	945.0
		0.00921	382.0			0.004338	113.0	0.01105	315.0	0.032746	968.0
		0.00963	389.0			0.004912	118.0	0.01252	331.0	0.037032	1010
		0.01001	396.0					0.01347	342.0		
		0.01038	402.0					0.01461	355.0		
		0.01135	419.0					0.01572	368.0		
		0.01217	434.0					0.01702	380.0		
		0.01310	452.0								
		$w_1 = 0.20$						$w_1 = 0.50$			
CTAB		TTAB		DTAB		CTAB		TTAB		DTAB	
0.000164	10.7	0.00071	41.7	0.002135	128.0	0.000259	8.42	0.00086	24.9	0.003250	90.8
0.000319	19.6	0.00138	81.1	0.004138	243.0	0.000503	14.8	0.00167	47.4	0.006303	171.0
0.000464	28.0	0.00201	116.0	0.006022	348.0	0.000732	21.3	0.00243	68.3	0.009176	246.0
0.000601	35.8	0.00261	148.0	0.007797	446.0	0.000948	27.2	0.00315	88.1	0.011886	314.0
0.000731	43.3	0.00317	180.0	0.009472	535.0	0.001152	32.7	0.00383	105.0	0.014444	378.0
0.000853	50.4	0.00370	209.0	0.011054	619.0	0.001345	38.1	0.00447	122.0	0.016865	436.0
0.000969	57.3	0.00421	236.0	0.012553	697.0	0.001528	43.1	0.00508	138.0	0.019158	492.0
0.001080	63.8	0.00469	257.0	0.013974	771.0	0.001702	47.9	0.00566	153.0	0.021333	544.0
0.001184	69.8	0.00514	269.0	0.015322	840.0	0.001867	52.5	0.00621	167.0	0.023400	592.0
0.001284	74.8	0.00558	279.0	0.016604	901.0	0.002024	56.8	0.00674	180.0	0.025366	636.0
0.001379	77.9	0.00599	287.0	0.017825	951.0	0.002173	60.8	0.00724	193.0	0.027238	678.0
0.001469	80.0	0.00638	294.0	0.018988	983.0	0.002315	64.6	0.00771	204.0	0.029023	717.0
0.001556	81.7	0.00676	300.0	0.020097	1000	0.002451	68.2	0.00817	215.0	0.030727	753.0
0.001638	83.1	0.00712	305.0	0.021157	1020	0.002581	71.7	0.00860	226.0	0.032355	786.0
0.001793	85.8	0.00779	316.0	0.022170	1040	0.002706	75.0	0.00902	237.0	0.033913	817.0
0.001935	88.2	0.00841	325.0	0.023139	1060	0.002825	78.1	0.00942	247.0	0.035404	838.0
0.002066	90.3	0.00899	333.0	0.024958	1090	0.003048	84.0	0.01017	265.0	0.036833	865.0
0.002188	91.0	0.00951	341.0	0.026633	1120	0.003254	89.4	0.01086	280.0	0.038204	892.0
0.002300	93.0	0.01001	348.0	0.028180	1140	0.003444	94.0	0.01150	293.0	0.040784	938.0
0.002604	99.0	0.01134	367.0	0.032247	1200	0.003621	98.0	0.01209	303.0	0.043169	979.0
		0.01297	391.0	0.035547	1260	0.003785	102.0	0.01265	312.0	0.045381	1005
		0.01449	414.0			0.003938	106.0	0.01316	320.0	0.047438	1030
						0.004081	109.0	0.01364	327.0	0.049355	1050
						0.004214	111.0	0.01409	332.0	0.051147	1070
						0.004340	113.0	0.01452	337.0	0.052825	1087
						0.004685	118.0	0.01570	350.0	0.054399	1101
						0.005010	120.0	0.01667	358.0	0.058718	1147
						0.005260	122.0	0.01753	365.0		
						0.005790	127.0	0.01876	378.0		
						0.006360	133.0				

Table 2. Conductivities and Corresponding Molarities of Alkyltrimethylammonium Bromides in EG (1) + Water (2) Mixtures with $w_1 = 0.30$ at (303.15, 308.15, 313.15, 318.15, and 323.15) K

$\frac{C}{\text{mol}\cdot\text{dm}^{-3}}$	$\frac{\kappa}{\mu\text{S}\cdot\text{cm}^{-1}}$	$\frac{C}{\text{mol}\cdot\text{dm}^{-3}}$	$\frac{\kappa}{\mu\text{S}\cdot\text{cm}^{-1}}$	$\frac{C}{\text{mol}\cdot\text{dm}^{-3}}$	$\frac{\kappa}{\mu\text{S}\cdot\text{cm}^{-1}}$	$\frac{C}{\text{mol}\cdot\text{dm}^{-3}}$	$\frac{\kappa}{\mu\text{S}\cdot\text{cm}^{-1}}$	$\frac{C}{\text{mol}\cdot\text{dm}^{-3}}$	$\frac{\kappa}{\mu\text{S}\cdot\text{cm}^{-1}}$	$\frac{C}{\text{mol}\cdot\text{dm}^{-3}}$	$\frac{\kappa}{\mu\text{S}\cdot\text{cm}^{-1}}$
$T = 303.15$ K						$T = 318.15$ K					
CTAB		TTAB		DTAB		CTAB		TTAB		DTAB	
0.000274	15.4	0.000893	48.3	0.002918	151.8	0.000343	27.5	0.001433	106.7	0.003202	225.0
0.000531	29.2	0.001732	90.6	0.005657	282.0	0.000665	50.9	0.002783	199.5	0.006214	429.0
0.000774	41.6	0.002523	129.6	0.008234	401.0	0.000969	72.8	0.004057	282.0	0.009050	614.0
0.001003	53.0	0.003269	165.9	0.010663	513.0	0.001256	93.2	0.005262	361.0	0.011727	783.0
0.001219	64.0	0.003974	199.0	0.012956	616.0	0.001528	112.6	0.006402	435.0	0.014257	938.0
0.001423	74.4	0.004642	228.0	0.015124	711.0	0.001785	130.5	0.007483	500.0	0.016652	1084
0.001617	84.1	0.005275	257.0	0.017177	799.0	0.002029	148.1	0.008509	551.0	0.018923	1220
0.001801	93.0	0.005876	283.0	0.019125	882.0	0.002261	164.3	0.009484	589.0	0.021079	1346
0.001976	99.9	0.006447	302.0	0.020974	956.0	0.002481	179.1	0.010412	618.0	0.023128	1467
0.002142	104.0	0.006991	318.0	0.022733	1021	0.002692	190.9	0.011297	642.0	0.025079	1574
0.002300	107.0	0.007509	330.0	0.024407	1069	0.002892	198.6	0.012141	662.0	0.026937	1668
0.002451	109.5	0.008003	339.0	0.026003	1105	0.003083	203.1	0.012947	680.0	0.028711	1749
0.002596	111.7	0.008475	347.0	0.027526	1136	0.003266	206.1	0.013718	698.0	0.030404	1817
0.002733	114.1	0.008927	355.0	0.028981	1162	0.003440	210.0	0.014455	715.0	0.032024	1874
0.002865	116.0	0.009359	362.0	0.030372	1187	0.003608	215.0	0.015162	730.0	0.033573	1927
0.002992	118.1	0.009772	367.0	0.031704	1208	0.003768	219.0	0.015839	745.0	0.035057	1973
0.003229	121.6	0.010550	378.0	0.034204	1246	0.004070	228.0	0.017113	772.0	0.037846	2070
0.003448	124.7	0.011267	389.0	0.036506	1284	0.004348	232.0	0.018291	795.0	0.040418	2140
0.003650	128.0	0.011930	398.0	0.038635	1316	0.004605	239.0	0.021565	856.0	0.042798	2200
0.003838	130.6	0.012546	406.0	0.040607	1346	0.004845	243.0			0.045006	2260
0.004346	137.2	0.014224	428.0	0.042441	1374	0.005507	257.0			0.051028	2400
				0.044149	1398					0.055935	2510
				0.045746	1421						
				0.050056	1480						
$T = 308.15$ K						$T = 323.15$ K					
CTAB		TTAB		DTAB		CTAB		TTAB		DTAB	
0.000348	22.2	0.000877	52.9	0.002736	160.5	0.000431	36.3	0.001391	111.7	0.0034	262
0.000676	41.6	0.001702	99.8	0.005305	296.0	0.000836	68.6	0.002699	206.0	0.006595	501
0.000984	59.5	0.002479	143.0	0.007722	424.0	0.001218	99.4	0.003933	295.0	0.009604	717
0.001275	76.3	0.003213	183.4	0.010000	541.0	0.001578	127.5	0.005099	380.0	0.012441	918
0.001550	91.8	0.003906	217.0	0.012150	650.0	0.001919	154.5	0.006201	457.0	0.015123	1100
0.001810	107.0	0.004562	252.0	0.014184	751.0	0.002242	179.0	0.007246	526.0	0.017660	1272
0.002057	120.0	0.005184	285.0	0.016109	844.0	0.002548	201.0	0.008237	592.0	0.020065	1427
0.002292	128.0	0.005775	316.0	0.017935	932.0	0.002838	220.0	0.009178	647.0	0.022347	1574
0.002514	133.4	0.006336	342.0	0.019670	1014	0.003115	235.0	0.010073	691.0	0.024516	1708
0.002727	137.7	0.006871	364.0	0.021319	1089	0.003378	246.0	0.010926	725.0	0.026579	1833
0.002929	141.6	0.007380	382.0	0.022889	1158	0.003629	254.0	0.011739	753.0	0.028545	1949
0.003121	145.0	0.007866	396.0	0.024386	1218	0.003868	262.0	0.012515	776.0	0.030420	2070
0.003306	148.7	0.008330	406.0	0.025814	1267	0.004097	268.0	0.013257	797.0	0.032211	2170
0.003482	151.6	0.008773	417.0	0.027179	1307	0.004316	274.0	0.013967	817.0	0.033922	2250
0.003650	154.5	0.009198	425.0	0.028484	1342	0.004525	280.0	0.014646	835.0	0.035559	2320
0.003811	157.6	0.009604	432.0	0.029733	1369	0.004726	285.0	0.015297	852.0	0.037127	2380
0.004115	162.3	0.010368	446.0	0.032077	1417	0.005103	295.0	0.016520	882.0	0.040071	2480
0.004394	167.0	0.011073	458.0	0.034236	1459	0.005450	304.0	0.017650	909.0	0.042786	2570
0.005149	178.4	0.011725	468.0	0.036232	1494	0.005772	313.0	0.018696	934.0	0.045297	2650
		0.012330	479.0	0.038082	1531	0.006071	319.0	0.019667	958.0	0.047626	2720
		0.012893	488.0	0.039802	1561	0.006893	339.0	0.022357	1014	0.053929	2880
		0.013418	497.0	0.041404	1591			0.024546	1062		
		0.014863	517.0	0.042901	1617						
				0.046944	1677						
$T = 313.15$ K											
CTAB		TTAB		DTAB							
0.000367	25.8	0.001020	68.5	0.003328	209.0						
0.000712	48.5	0.001979	130.1	0.006455	396.0						
0.001036	69.2	0.002883	186.6	0.009397	566.0						
0.001343	88.4	0.003737	234.0	0.012171	720.0						
0.001633	106.7	0.004544	282.0	0.014792	863.0						
0.001907	123.8	0.005309	329.0	0.017270	997.0						
0.002167	140.0	0.006034	370.0	0.019618	1121						
0.002414	153.1	0.006722	408.0	0.021846	1237						
0.002649	161.6	0.007377	440.0	0.023963	1340						
0.002872	167.4	0.008000	467.0	0.025976	1432						
0.003085	172.5	0.008594	485.0	0.027893	1508						
0.003288	176.8	0.009161	501.0	0.029721	1567						
0.003482	181.2	0.009703	514.0	0.031466	1620						
0.003667	184.7	0.010221	527.0	0.033133	1661						
0.003845	188.7	0.010717	538.0	0.034728	1703						
0.004015	191.7	0.011192	547.0	0.036255	1738						
0.004334	197.7	0.011647	557.0	0.039122	1799						
0.004629	203.0	0.012084	566.0	0.041765	1855						
0.004901	209.0	0.012504	573.0	0.044208	1906						
0.005154	214.0	0.012908	582.0	0.046473	1952						
0.005844	225.0	0.013671	595.0	0.052554	2090						
		0.014378	608.0								
		0.015037	620.0								
		0.016856	650.0								

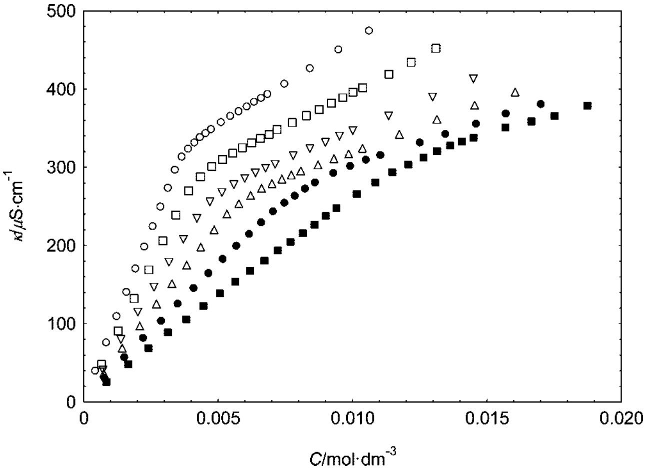

Figure 1. Conductivity (κ) versus concentration of tetradecyltrimethylammonium bromide (C) in EG (1) + water (2) mixtures at 298.15 K: ○, water; □, $w_1 = 0.10$; ▽, $w_1 = 0.20$; △, $w_1 = 0.30$; ●, $w_1 = 0.40$; ■, $w_1 = 0.50$.

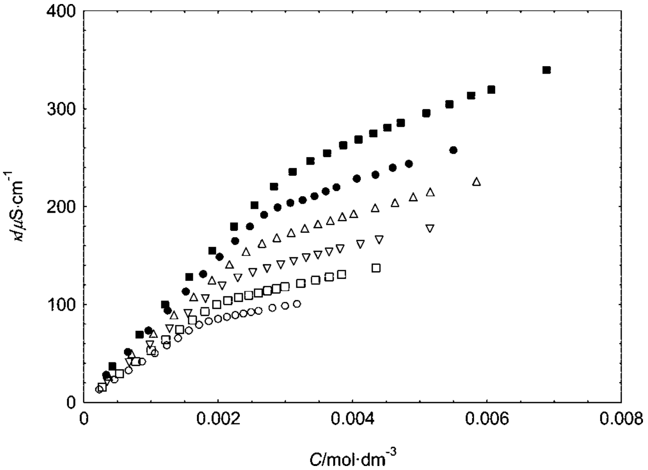

Figure 2. Conductivity (κ) versus concentration of hexadecyltrimethylammonium bromide (C) in EG (1) + water (2) mixtures at different temperatures: ○, 298.15 K; □, 303.15 K; ▽, 308.15 K; △, 313.15 K; ●, 318.15 K; ■, 323.15 K.

TTAB in EG (1) + water (2) mixtures with higher EG content. Finally, once ΔG^0_m and ΔH^0_m have been calculated, the entropic contribution, $T\Delta S^0_m$, may be determined from

$$T\Delta S^0_m = \Delta H^0_m - \Delta G^0_m \tag{7}$$

In addition, the effect of a cosolvent or additive on the micellization process can be studied by means of the Gibbs energy of transfer (ΔG^0_{trans}) defined by[31]

$$\Delta G^0_{trans} = (\Delta G^0_m)_{EG+H_2O} - (\Delta G^0_m)_{H_2O} \tag{8}$$

The standard Gibbs energies of micellization (ΔG^0_m) and the Gibbs energies of transfer (ΔG^0_{trans}) for the three surfactants studied in EG (1) + water (2) mixtures at 298.15 K are given in Table 3. From this table, it can be seen that the micellization becomes less spontaneous upon addition of an increasing amount of EG to water. The different thermodynamic parameters of these surfactants in a given EG (1) + water (2) mixture with $w_1 = 0.30$ are given in Table 4. Our results show that the degree of counterion dissociation (α) of micelle for all these three surfactants increases with temperature as found earlier for other cationic surfactants[32,33] in aqueous solutions. The Gibbs energies of micellization are, in all cases, negative and become slightly more negative for CTAB as the temperature increases, whereas a reverse trend is observed for TTAB and DTAB where ΔG^0_m values slowly increase with temperature. This behavior suggests that aggregation of these surfactants in the EG (1) + water (2) mixture with $w_1 = 0.30$ is almost independent of temperature.

Table 3. Critical Micellar Concentration (cmc), Degree of Counterion Dissociation (α), Gibbs Energy of Micellization (ΔG^0_m), and Gibbs Energy of Transfer (ΔG^0_{trans}) Values for Alkyltrimethylammonium Bromides in EG (1) + Water (2) Mixtures at 298.15 K[a]

w_1	cmc / mol·dm^{-3}	α	$-\Delta G^0_m$ / kJ·mol^{-1}	ΔG^0_{trans} / kJ·mol^{-1}
		CTAB		
0.00	0.93	0.269	47.19	
0.10	1.14	0.276	45.85	1.34
0.20	1.33	0.279	44.81	2.38
0.30	1.79	0.284	43.10	4.09
0.40	2.57	0.315	40.46	6.73
		TTAB		
0.00	3.74	0.250	41.67	
0.10	4.13	0.255	40.84	0.83
0.20	4.80	0.268	39.59	2.08
0.30	5.77	0.285	38.10	3.57
0.40	8.14	0.327	35.39	6.28
0.50	11.94	0.378	32.39	9.28
		DTAB		
0.00	14.47	0.261	35.58	
0.10	16.82	0.271	34.44	1.14
0.20	18.72	0.288	33.36	2.22
0.30	21.11	0.312	32.07	3.51
0.40	26.96	0.374	29.57	6.01
0.50	35.40	0.430	27.13	8.45

[a] The uncertainty limits of cmc, α, and ΔG^0_m are (± 3, ± 4, and ± 4) %, respectively.

Table 4. Thermodynamic Parameters for Micellization of Alkyltrimethylammonium Bromides in the EG (1) + Water (2) Mixture with $w_1 = 0.30$ at Different Temperatures[a]

T / K	10^3cmc / mol·dm^{-3}	α	$-\Delta G^0_m$ / kJ·mol^{-1}	$-\Delta H^0_m$ / kJ·mol^{-1}	$T\Delta S^0_m$ / kJ·mol^{-1}
			CTAB		
298.15	1.79	0.284	43.10	23.59	19.51
303.15	1.89	0.294	43.33	24.25	19.08
308.15	2.10	0.303	43.35	24.92	18.43
313.15	2.34	0.311	43.37	25.61	17.76
318.15	2.56	0.320	43.43	26.30	17.13
323.15	2.80	0.325	43.58	27.05	16.53
			TTAB		
298.15	5.77	0.285	38.10	25.57	12.53
303.15	6.22	0.299	38.09	26.21	11.88
308.15	6.88	0.308	38.08	26.94	11.14
313.15	7.68	0.315	38.06	27.71	10.35
318.15	8.46	0.326	38.00	28.41	9.59
323.15	9.51	0.333	37.89	29.19	8.70
			DTAB		
298.15	21.11	0.312	32.07	17.76	14.31
303.15	22.07	0.340	31.88	18.06	13.82
308.15	23.90	0.367	31.55	18.36	13.19
313.15	26.43	0.394	31.12	18.65	12.47
318.15	27.36	0.417	31.00	18.97	12.03
323.15	29.94	0.432	30.82	19.39	11.43

[a] The uncertainty limits of cmc, α, ΔG^0_m, ΔH^0_m, and ΔS^0_m are (± 3, ± 4, ± 4, ± 3, and ± 5) %, respectively.

Table 5. Values of the Free Energy ($\Delta G^0_{CH_2}$) for the Transfer of One Methylene (CH_2) Group from the Bulk Phase to the Micellar Pseudophase for Alkyltrimethylammonium Bromide Micellar Solutions in EG (1) + Water (2) Mixtures at 298.15 K

w_1	0.00	0.10	0.20	0.30	0.40	0.50
$\Delta G^0_{CH_2}$/kJ·mol^{-1}	2.92	2.87	2.84	2.69	2.59	2.37

Table 6. Surface Tension (γ), Molar Volume (V), and Gordon Parameter (G) for EG (1) + Water (2) Mixtures at 298.15 K

w_1	$10^3\gamma$ / $N \cdot m^{-1}$	V^a / $dm^3 \cdot mol^{-1}$	G / $J \cdot m^{-3}$
0.00	71.9	18.07	2.74
0.10	66.9	21.85	2.39
0.20	64.2	25.64	2.18
0.30	61.7	29.42	1.99
0.40	59.9	33.21	1.86
0.50	58.0	36.99	1.74
1.00	48.6	55.92	1.27

[a] Estimated considering $V = V_1x_1 + V_2(1 - x_1)$, where x_1 is the mole fraction of EG in the mixture and V_1 and V_2 are the molar volumes of EG and water, respectively.

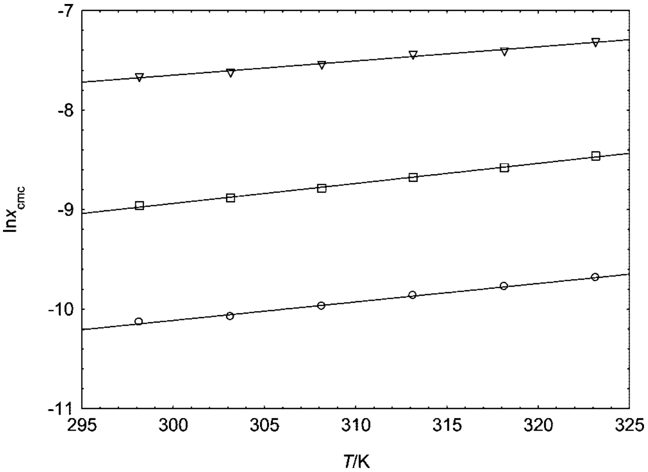

Figure 3. Plots of ln x_{cmc}versus temperature for different alkyltrimethylammonium bromides in EG (1) + water (2) mixture with $w_1 = 0.30$: ○, CTAB; □, TTAB; ▽, DTAB.

The enthalpy of micellization is negative and becomes more negative with increasing temperature. On the other hand, the $T\Delta S^0_m$ values are, in general, positive and becomes less positive as temperature increases. These results demonstrate that the micellization behavior of the alkyltrimethylammonium bromides in the EG (1) + water (2) mixture with $w_1 = 0.30$ is governed by the entropy−enthalpy compensation effect. Similar behavior has also been observed previously[34] for sodium dodecylsulfate in different binary aqueous mixtures.

The values of ΔG^0_{trans} estimated using eq 8 are listed in Table 3. For all surfactant systems investigated, the values of ΔG^0_{trans} were found to be positive. The positive values of ΔG^0_{trans} can be attributed to the reduction in the solvophobic interactions caused by the improved solvation, which leads to an increase in the solubility of the hydrocarbon tails in the presence of EG, and consequently there will be an increase in cmc.

The excess surface concentration (Γ_{max}) and the minimum area per surfactant molecules (A_{min}) at the air/solvent interface were obtained using the surface tension measurements from the following equations[35]

$$\Gamma_{max} = -\frac{1}{2RT}\left(\frac{\partial \gamma}{\partial \ln C}\right)_{T,p} \tag{9}$$

$$A_{min} = \frac{1}{N_A \Gamma_{max}} \tag{10}$$

where R is the gas constant; N_A is Avogadro's number; γ is the surface tension; and C is the concentration of surfactant in solution. The values of the surface pressure at the cmc (Π_{cmc}) were obtained by using the following equation

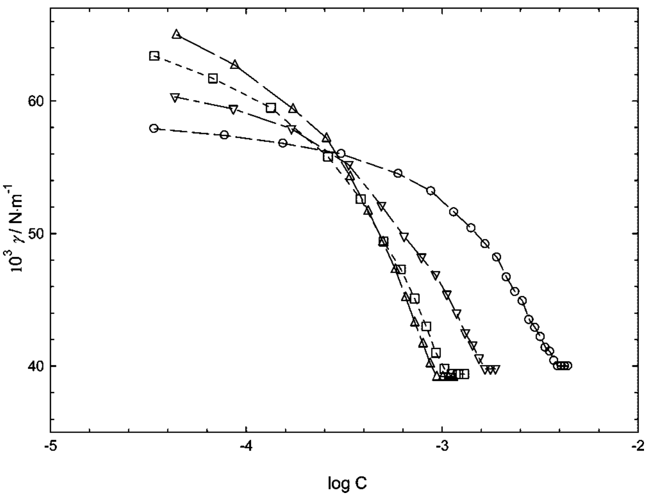

Figure 4. Variation of γ with log C for CTAB in different EG (1) + water (2) mixtures at 298.15 K: △, water; □, $w_1 = 0.10$; ▽, $w_1 = 0.30$; and ○, $w_1 = 0.50$.

Table 7. Critical Micellar Concentration (cmc), Excess Surface Concentration (Γ_{max}), Minimum Area Per Molecule (A_{min}), Surface Pressure at the cmc (Π_{cmc}), and Gibbs Energy of Adsorption (ΔG^0_{ads}) for Alkyltrimethylammonium Bromides in EG (1) + Water (2) Mixtures at 298.15 K

100 w_1	10^3cmc / $mol \cdot dm^{-3}$	$10^6\Gamma_{max}$ / $mol \cdot m^{-2}$	$10^{20}A_{min}$ / m^2	$10^3\Pi_{cmc}$ / $N \cdot m^{-1}$	$-\Delta G^0_{ads}$ / $kJ \cdot mol^{-1}$
		CTAB			
0	0.94	0.705	236	32.80	93.71
10	1.11	0.595	278	27.54	92.14
30	1.66	0.500	332	21.88	86.86
50	3.86	0.470	354	17.98	75.68
		TTAB			
0	3.80	0.525	316	38.41	114.83
10	4.14	0.395	420	32.55	123.24
30	5.33	0.285	582	27.94	136.13
50	10.69	0.200	830	20.79	136.34
		DTAB			
0	11.44	0.495	334	40.20	116.79
10	13.07	0.360	462	34.88	131.33
30	16.97	0.255	650	27.85	141.29
50	28.35	0.180	898	19.36	134.69

$$\Pi_{cmc} = \gamma_0 - \gamma_{cmc} \tag{11}$$

where γ_0 is the surface tension of the solvent and γ_{cmc} is that of the surfactant solution at the cmc.

Finally, the Gibbs energy of adsorption (ΔG^0_{ads}) was determined from

$$\Delta G^0_{ads} = \Delta G^0_m - \frac{\Pi_{cmc}}{\Gamma_{max}} \tag{12}$$

where the standard state in the surface phase is defined as the surface covered with a monolayer of surfactant at a surface pressure equal to zero. The dependence of surface tension with the logarithm of the molar concentration of CTAB is shown in Figure 4. The values of cmc, Γ_{max}, A_{min}, and ΔG^0_{ads} are listed in Table 7. The cmc values obtained by surface tension measurements are in good agreement with those obtained from conductometric measurements. One can notice that the values of Γ_{max} increase and those of A_{min} decrease, when the length of the hydrocarbon chain increases. It shows that the more hydrophobic the surfactant molecules are, the stronger is the tendency of those molecules to escape from the solvent to the air/solvent interface (there is less affinity between solvent and surfactant molecules), resulting in a more packed surface. An increase in the amount of EG in the EG (1) + water (2) mixtures results in a decrease in $\Gamma_{\max}$ and an increase in $A_{\min}$. This indicates an increased solubilization of EG into the micelles leading to an increase in the surface area per surfactant molecule as the solvent medium becomes richer in EG. All of the ΔG^0_{ads} values listed in Table 7 are negative, indicating that the adsorption of surfactant at the air/mixture interface takes place spontaneously. This process is also found to be more spontaneous as the hydrocarbon chain of the surfactant gets longer and as the medium becomes richer in water. Besides, ΔG^0_{ads} values are more negative than the corresponding ΔG^0_{m} values. This indicates that when a micelle is formed work needs to be done to transfer the surfactant molecules in the monomeric form at the surface to the micellar state in the mixed solvent media.[36]

Conclusions

The critical micelle concentrations and the micellar degree of counterion dissociation of the investigated alkyltrimethylammonium bromides, viz., hexadecyl-, tetradecyl-, and dodecyltrimethylammonium bromides in EG (1) + water (2) mixed solvent media are always found to be greater than the corresponding values in aqueous media. From the study of the temperature dependence of the cmc of these surfactants in the EG (1) + water (2) mixture with $w_1 = 0.30$, it has been demonstrated that the micellization is mainly governed by an enthalpy−entropy compensation effect. Data on the thermodynamics of adsorption demonstrate that the surface activity of these surfactant decreases with the addition of EG to water at a given temperature and that the adsorption of surfactant at the air/mixture interface takes place spontaneously.

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Received for review July 1, 2008. Accepted November 15, 2008.

JE8005024