Formation of Micelles of Hexadecyltrimethylammonium Bromide in Water–*N*,*N*-Dimethylformamide Solutions

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The critical micellar concentration of aqueous solutions of hexadecyltrimethylammonium bromide (HTAB) containing various amounts of *N*,*N*-dimethylformamide (DMF) has been determined at 25 and 40 °C by means of surface tensiometric measurements. The standard free energy ($\Delta G_m°$), enthalpy ($\Delta H_m°$), and entropy ($\Delta S_m°$) of micellization were also determined. The experimental results indicate that: (1) micelle formation is somewhat hindered by a raise in temperature, and (2) DMF has an inhibitory effect on the formation of micelles of HTAB. This effect is relatively small at low DMF concentrations, but it increases drastically as the mole fraction of DMF approaches 0.33. The changes in the $\Delta G_m°$, $\Delta H_m°$, and $\Delta S_m°$ values indicate that the formation of HTAB micelles in the water–DMF mixtures is an entropy directed process at lower concentrations of DMF and the inhibitory effect of DMF on micelle formation is attributed to an increase in the orderliness of this system with increasing DMF concentration.

N,*N*-Dimethylformamide (DMF) is a common dipolar aprotic solvent often used as a medium for many organic reactions. Other common dipolar aprotic solvents are dimethyl sulfoxide (DMSO), *N*,*N*-dimethylacetamide, acetone, tetrahydrofuran, sulfolane, and dioxane. They are usually weak hydrogen bond donors and very weakly acidic. On the contrary, they may often act as strong bases. Usually aprotic solvents contain hydrogen attached to carbon and are generally dipolar in nature.[1–3] Most of them are relatively miscible with water.

As part of our study of the effect of polar solvents on the formation of micelles in aqueous solutions, we decided to also investigate the effect of DMF on the micellization of hexadecyltrimethylammonium bromide (HTAB). Our previous studies of the HTAB–H_2O–DMSO system have revealed that the addition of DMSO has an inhibitory effect on the formation of micelles in aqueous solutions.[4–6] Surface tensiometric experiments indicated that DMSO increased the critical micellar concentration of HTAB in water at low concentrations.[4] At mole fractions of DMSO higher than 0.33 micelle formation did not appear to take place. The results of spin-lattice relaxation measurements for the terminal methyl, *N*-methyl, and methylene groups of hexadecyltrimethylammonium bromide substantiated these results and showed that when the DMSO concentration is equal to a mole fraction of 0.366 the surfactant monomer molecules are essentially isolated from each other by the increased "structuring" of the water–DMSO liquid system.[5–6] Spin-lattice relaxation and chemical shift measurements performed in our laboratory also indicated that this liquid system is in its most structured state through hydrogen bonding between water and DMSO molecules when the mole fraction of DMSO is about 0.35.[7]

The mixing of DMF with water is a strongly exothermic process with a maximum value at the mole fraction of 0.66 for H_2O, while the activity coefficients for water and DMF are relatively near unity.[8] In addition, a variety of other physical properties of water–DMF solutions exhibit extrema at a mole fraction of 0.66 for water.[9–11] On the basis of cryoscopic and calorimetric measurements of aqueous solutions of *N*,*N*-dimethylformamide, Bougard and Jadot[8] have concluded that DMF forms both the monohydrate ($DMF\cdot H_2O$) and the dihydrate ($DMF\cdot 2H_2O$) and that the association is probably mainly through hydrogen bonding.

We have decided to study in some detail the HTAB–H_2O–DMF system because of the vast information available in the literature for the surfactant and in order to compare it to the HTAB–H_2O–DMSO system that we have previously studied. The present work essentially involved the experimental evaluation of thermodynamic functions such as the free energy, enthalpy, and entropy of micellization from the critical micellar concentration (CMC) of HTAB in various water–DMF mixtures at 25 and 40 °C determined by means of surface tensiometry.

Experimental

The DMF used was of spectro quality and was obtained from Eastman Organic Chemicals, Cleveland, Ohio 44114. It was employed without any additional treatment or purification. Hexadecyltrimethylammonium bromide (HTAB), $CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$, was purchased from Aldrich Chemical Company, Milwaukee, Wisconsin 53233. It was recrystallized twice from 95% ethyl alcohol and dried under vacuum for two days. Doubly distilled water was used in the preparation of all the solutions.

The surface tension of HTAB-H_2O-DMF solutions was measured at 25 and 40 °C by means of a Fisher Model 21 Semi-Automatic Tensiometer. The solutions were prepared gravimetrically at the following mole fractions of DMF: 0.000, 0.025, 0.055, 0.091, 0.134, 0.188, 0.258, and 0.351. All of them contained at least fifteen different concentrations of HTAB. Ten milliliter aliquots of the solutions were measured in a Petri dish with a diameter of 6 cm. The tensiometer was set at a constant height. The final surface tension of any solution was the average of at least three measurements.

The CMC's were determined from plots of the surface tension of the solutions *versus* the logarithm of the concentration of HTAB. The marked change in the plots is taken as an indication of micelle formation and the inflection

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Table 1. Critical micellar concentration of hexadecyltrimethylammonium bromide in aqueous solutions containing different mole fractions of *N*,*N*-dimethylformamide

Mole fraction of DMF	Critical micellar concentration at 25 °C ($M\times10^3$)	Critical micellar concentration at 40 °C ($M\times10^3$)
0.0	0.92	1.00
0.025	2.00	2.24
0.055	3.55	3.98
0.091	6.31	7.08
0.134	10.0	11.5
0.188	12.6	20.0
0.258	29.5	—
0.351	—	—

Table 2. Some thermodynamic properties for the formation of micelles of hexadecyltrimethylammonium bromide in water-*N*,*N*-dimethylformamide solutions

Mole fraction of DMF	$\Delta H_m°$ kcal mol^{-1}	$\Delta G_m°$ at 25 °C kcal mol^{-1}	$\Delta S_m°$ at 25 °C e.u.
0.0	—	−4.12	—
0.025	−1.37	−3.68	+7.75
0.055	−1.37	−3.34	+6.61
0.091	−1.49	−3.00	+5.06
0.134	−1.73	−2.73	+3.35
0.188	−5.73	−2.59	−10.6
0.258	—	−2.09	—

point in the curve is considered to correspond to the CMC. Linear plots are taken as an indication that micelle formation does not occur.

Results and Discussion

Some representative experimental results obtained for the surface tension of different HTAB solutions in various water–DMF mixtures at 25 °C are given in Fig. 1. Most plots of surface tension *versus* the logarithm of the concentration of HTAB exhibit an initial marked drop and subsequently level off. Similar results have been obtained for the same solutions at 40 °C. The CMC values thus determined for the different H_2O–DMF mixtures are summarized in Table 1.

As can be seen from Table 1, the effect of DMF on micelle formation is relatively small at low concentrations of DMF, but it increases drastically as the mole fraction of DMF approaches 0.33. This mole fraction corresponds to the formation of the stoichiometric hydraote $DMF\cdot 2H_2O$.[8] At mole fractions of DMF higher than 0.33, the formation of HTAB micelles does not appear to take place in similarity to the HTAB–H_2O–DMSO system.[4–6] We have shown conclusively by means of proton spin-lattice relaxation measurements that this was true for the latter system.[4–6]

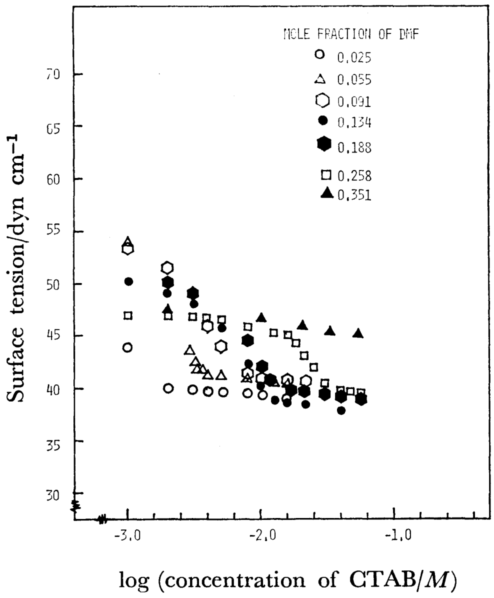

Fig. 1. Dependence of surface tension on the logarithm of the concentration of hexadecyltrimethylammonium bromide in water-*N*,*N*-dimethylformamide solutions at 25 °C.

The thermodynamics of micelle formation has been discussed and treated extensively in the literautre.[12–14] One approach assumes that the process of micellization involves the formation of a distinct micellar phase at the CMC and that the concentration of monomers in solution is constant, once micelles are formed. Then, the standard free energy of micellization, $\Delta G_m°$, is given by the following equation to a good approximation:

$$\Delta G_m° = RT\ln \mathrm{CMC}. \tag{1}$$

If one assumes that the aggregation number and the degree of ionization of the surfactant are temperature independent, the standard enthalpy ($\Delta H_m°$) and entropy ($\Delta S_m°$) of micellization can be evaluated by temperature dependence of the CMC and the Gibbs-Helmholtz relationship. The values thus determined for $\Delta G_m°$ for the fomation of HTAB micelles in variuos water–DMF solutions at 25 °C are given in Table 2. The more approximate $\Delta H_m°$ and $\Delta S_m°$ quantities, calculated on the basis of the measurements at two temperatures only, are also shown in the same table. The experimental results show that micelle formation is slightly hindered by increasing the temperature from 25 to 40 °C. The results also indicate that the addition of DMF has an inhibitory effect on the formation of micelles of HTAB in aqueous solutions. This effect due to the cosolvent is more pronounced than the one that we have observed for dimethyl sulfoxide.[4–6] Figure 2 illustrates a comparison of the effects of DMF and DMSO at 25 °C in terms of $\Delta G_m°$.

The $\Delta G_m°$ values determined for micelle formation in the water–DMF mixed solvent system vary almost linearly from −3.68 to −2.09 kcal/mol with increasing concentration of DMF and are always less negative than those determined for the formation of HTAB micelles in pure water (Table 2). The approximate enthalpy of micellization calculated, $\Delta H_m°$, is exothermic and almost constant at concentrations of DMF betweeen 0.025 and 0.134 mole fractions. The corresponding values of the entropy of micellization,

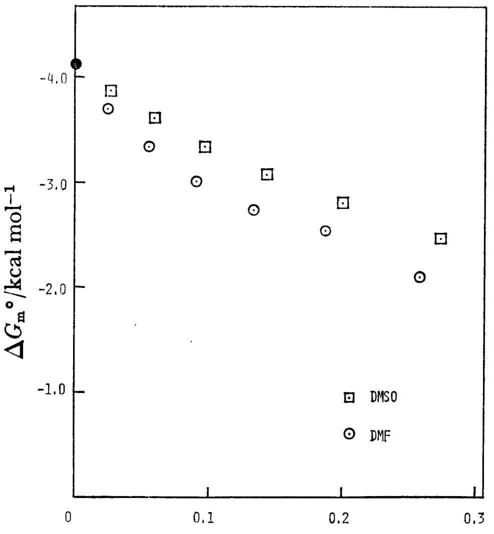

Fig. 2. Depence of the free energy of Micellization of hexadecyltrimethylammonium bromide at 25 °C on the composition of the water–dimethyl sulfoxide and water–*N*,*N*-dimethylformamide binary liquid systems.

$\Delta S_m°$, decrease gradually from 7.75 to 3.35 e.u. This means that the negative free energy of micellization is mainly due to the contribution of the entropy term in the H_2O–DMF mixed solvent system at low concentrations of DMF. This is in agreement with the general concept that micelle formation in aqueous solutions is an entropy directed process and arises mainly from the break-up of the "Frank-Evans microcrystals" of the ordered water structure by the surfactant molecules, even though the formation of aggregates by surfactant molecules is an entropy decreasing process. Since the $\Delta S_m°$ values decrease with increasing concentration of DMF (Table 2), an increase in the orderliness of the HTAB–H_2O–DMF system takes place as the mole fraction of DMF is increased. This is consistent with a strong interaction, such as hydrogen bonding, between water and DMF. As already mentioned, Bougard and Jadot[8] have confirmed the existence of the stoichiometric hydrate DMF·$2H_2O$ and suggested the presence of hydrogen bonding.

A further addition of DMF caused a significant change in the relative contributions from enthalpy and entropy, *i.e.*, at 0.188 mole fraction of DMF $\Delta H_m°$ and $\Delta S_m°$ become −5.73 kcal/mol and −10.6 e.u., respectively. A change similar to this was also observed in the water–DMSO mixed solvent system when the DMSO mole fraction was 0.275. This change implies that the driving force for micellization in both the H_2O–DMF and H_2O–DMSO mixed solvent systems containing higher concentrations of DMF or DMSO must be attributed to the enthalpic term. Why this change occurs at lower concentrations of DMF than DMSO may be explained by the fact that DMF has a more pronounced effect on the disruption of the water structure through hydrogen bonding, even though DMF is less polar than DMSO[15] (the dielectric constant of DMF at 25 °C is 36.7 while that of DMSO is 46.4). Altogether, the inhibitory effect of *N*,*N*-dimethylformamide on micelle formation can be explained in terms of a decrease of hydrophobic forces in the ternary system due to interactions between water and the cosolvent.

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