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# Thermodynamics of micelle formation of some cationic surfactants as a function of temperature and solvent

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The critical micelle concentrations (CMC) of some cationic surfactants, such as dodecyl, tetradecyl, hexadecyl (cetyl) trimethyl ammonium bromide, hexadecyl pyridinium chloride, hexadecyl dimethylethyl ammonium bromide and benzalkonium chloride has been determined over the temperature range 308-338 K by the electrical conductivity method. The counterion binding and thermodynamics of micellization ($\Delta G^\circ_m$, $\Delta S^\circ_m$, $\Delta H^\circ_m$) have been quantitatively determined. The micellar behaviour of hexadecyltrimethyl ammonium bromide have also been studied in dioxane-water solutions. A comparison with micelle formation for HTAB in other binary solvents, namely DMSO, DMF, methanol, ethanol, isopropanol, acetonitrile and THF has been made and discussed.

The formation of micelles is a cooperative process which occurs at a critical micelle concentration (CMC), characteristic of the surfactant species and various factors such as temperature, salt, solvent and pH of the solution. The CMC can serve as a measure of micelle stability in a given state, the thermodynamic properties of micellization can be determined from a study of the temperature dependence of the CMC. In continuation of our interest in the kinetics of hydrolysis of hydroxamic acids in micellar environment[1-4] we decided to study micellar properties of some cationic surfactants, which are very useful for kinetic studies. Extensive investigations on the thermodynamics of micellization of cationic and anionic surfactants have been reported, recently[5-16], but understanding even in this important area is still fragmentary. The various effective perturbants such as counterions, temperature, salt, solvents, etc. remain a matter of continued research interest. The availability of these thermodynamic parameters at various temperatures can give valuable insight into the principles which govern the formation of micelles. Significant contributions of Evans *et al.*[13,14], deserve special mention in this context.

In the present paper we report the results of our study on the temperature dependence of CMC some cationic surfactants namely dodecyl, tetradecyl and hexadecyl trimethyl ammonium bromide $C_{12}H_{25}N^+(CH_3)_3Br$ (DTAB), $C_{14}H_{29}N^+(CH_3)_3Br$ (TTAB), $C_{16}H_{33}N^+(CH_3)_3Br$ (CTAB), hexadecyl pyridinium halide $C_{16}H_{33}N^+\ C_5H_5Cl$ [CPC], $C_{16}H_{33}N^+\ C_2H_5Br$ [CPB] hexadecyl dimethyl ethyl ammonium bromide($C_{16}H_{33}N^+(CH_3)_2\ C_2H_5Br$ (CDEAB) and benzalkonium chloride ($C_{12}H_{25}N^+(CH_3)_3C_7H_7Cl$ BC) which have been obtained from conductance measurement in the 35 - 65°C temperature range at 10°C intervals. We have also analyzed in details the effect of dioxane on the formation of micelles of CTAB in aqueous solutions. Dioxane is a rather common organic solvent and is often used as a medium for many organic reactions. It belongs to the general group of aprotic solvents such as DMSO, DMF, THF, $CH_3CN$. An attempt is made to study thermodynamics of micellization of CTAB in these solvents and protic solvents (MeOH and PrOH ) for comparison.

## Materials and Methods

The surfactants were products of Aldrich. Fluka and BDH and were used without further purification. Surfactant solutions of a definite concentration were always freshly prepared by weighing out a certain amount of surfactant and diluting it upto the required volume with double distilled water. Dioxane (Qualigens AR), DMSO (Qualigens AR), DMF (Glaxo AR), THF (Merck), acetonitrite, MeOH, PrOH (Glaxo AR) were used as such. Conductance measurement were taken with a Systronics digital conductometer (Type 304).

The CMC was determined by the conventional conductivity method from the intersection of two lines on the plots of specific conductivity vs concentration (Figures 1 and 2). From the temperature dependence of *f* as well as CMC, Gibbs free energy $\Delta G^{\circ}_{m}$ , and enthalpy $\Delta H^{\circ}_{m}$ and entropy $\Delta S^{\circ}_{m}$, on micelle formation, were estimated for the respective surfactants .

## Results and Discussion

Micellization depends upon electrostatic repulsions and hydrophobic interactions. The

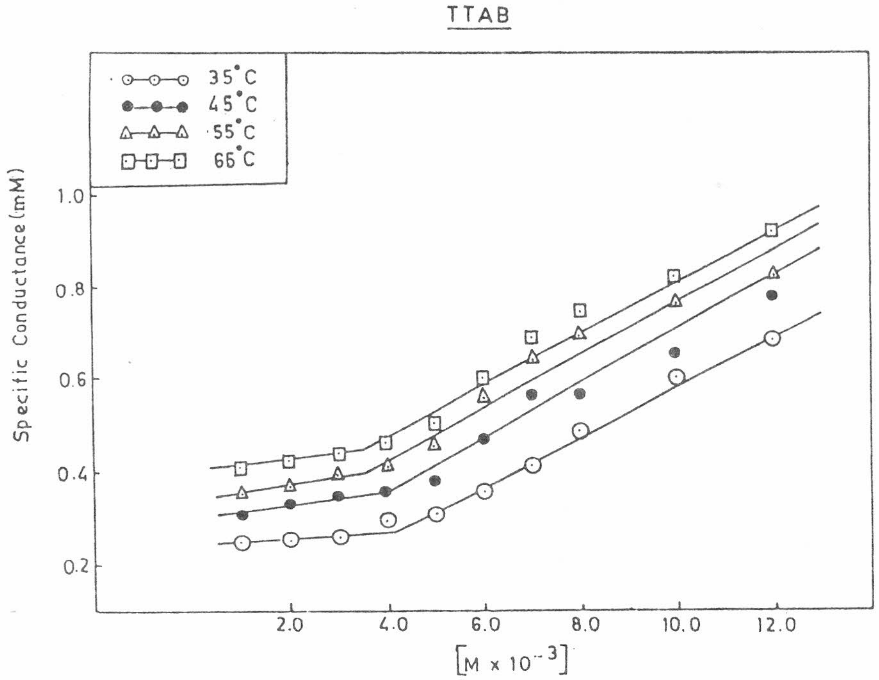

Figure 1 — Plot of specific conductivity vs concentration

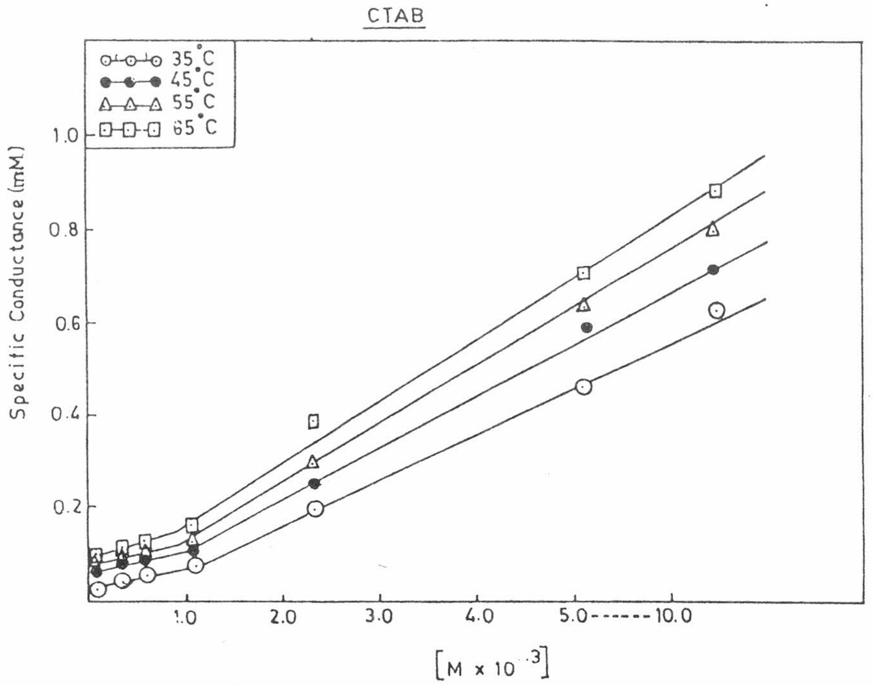

Figure 2 — Plot of specific conductivity vs concentration

importance of one of the two factors can be obtained from the studies of the thermodynamic properties of the micellization in which surfactant's alkyl chains, head groups, counterions and the medium all play vital roles.

Specific conductivities against concentrations are plotted for various temperatures, from which the CMC values are determined. The choice of CMC is never unambiguous, since the change in slope occurs, over a more or less narrow range of concentrations. It is obvious that CMC and hence CMC - derived parameters should depend on the methodology adopted. The results are presented in Table I. The effect of temperature on CMC is complex. Numerous changes in CMC with temperature for ionic surfactants are known [5-16]. Very few of these take place above 100°C however, the studies of the effects of temperature on micellization have mostly been limited to lower temperatures. The CMC of ionic surfactants generally passes through a minimum at $T_m$ with increasing temperature. In many cases the dependence is highly irregular. The nature of this effect is hard to predict because it depends on a series of factors, such as degree of counterion binding to micelle, molecular charge, restructuring of water and the interaction between water and the surfactant. Our observation can be explained in terms of the two interactions responsible for the micellization, i.e. ., hydrophobic interactions and break-up of the water structure with increasing temperature, the unique ordered structure of water diminishes and water becomes a more normal polar fluid. At lower temperature, the effect is exactly the contrary. The net result is a balancing of the two effects in the temperature range studied. For each system CMC decreases as temperature increases. The length of the hydrocarbon chain in a surfactant has been shown to be a major factor in guiding the CMC. In a homologous series, the CMC normally decreases logarithmically with the number of carbon atoms. It is observed (Table I) that as the chain length of the alkyl group of the surfactant increases (dodecyl to hexadecyl), the CMC decreases. Rakshit *et al.*[17]studied thermodynamics of micellization of some new pyrimidinium cationic surfactants. For each system CMC decreased with the increase in temperature.

Ionic micelles bind a considerable amount of counterions, which can be estimated by electrochemical measurements. Following the procedure of Evans[18] the counterion association ($f$), properties of surfactants have been evaluated from the ratio of the postmicellar and premicellar slopes obtained from the plots of specific conductance of the surfactant solution at different concentrations. The results are presented in Table I. Lengthening of the alkyl chain initially hinders micelle formation, but longer chains are markedly effective in lowering the CMC and increasing the aggregation number, owing to enhanced hydrophobic interaction between the counterion and micellar core. Counterion binding, increases with increasing alkyl chain length.

## Thermodynamics of micellization

Thermodynamic quantities of micellization like the Gibbs free energy $\Delta G^{\circ}_{m}$, the enthalpy $\Delta H^{\circ}_{m}$ and the entropy $\Delta S^{\circ}_{m}$, can be derived from the temperature dependence of CMC. The standard free energy of micellization per mole of monomer unit ($\Delta G^{\circ}_{m}$) of surfactants is related to the CMC by the relations as shown in Eqn. (1)

$$\Delta G^{\circ}_{m}=(1+f)\,RT\ln \mathrm{CMC} \qquad \ldots (1)$$

**Table I**—Critical micelle concentration and degree of counterion binding as a function of temperature

| Surfactants | CMC(mM) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 308 K | | 318 K | | 328 K | | 338 K | |
| | *f*% | *f*% | *f*% | *f*% | *f*% | *f*% | *f*% | *f*% |
| DTAB | 11.9 | 65.0 | 10.8 | 67.8 | 10.2 | 67.8 | 9.40 | 78.4 |
| TTAB | 4.10 | 60.0 | 4.00 | 75.0 | 3.80 | 75.0 | 3.74 | 81.8 |
| CTAB | 1.30 | 70.0 | 1.20 | 70.0 | 1.10 | 71.0 | 1.00 | 72.0 |
| CTACl | 2.00 | 71.4 | 1.80 | 71.4 | 1.40 | 71.4 | 1.00 | 71.4 |
| CDEAB | 1.75 | 71.4 | 1.70 | 81.2 | 1.60 | 81.2 | 1.48 | 84.6 |
| CPC | 1.00 | 60.0 | 0.80 | 69.2 | 0.75 | 74.2 | 0.60 | 74.2 |
| CPB | 1.74 | 63.0 | 1.40 | 70.0 | 1.35 | 70.0 | 1.20 | 70.0 |
| BC | 2.00 | 96.0 | 2.10 | 96.0 | 0.90 | 96.0 | 0.80 | 96.0 |

Using the CMC and the '*f*' values presented in Table I, the $\Delta G^{\circ}_{m}$ values for the studied surfactant systems have been computed and listed in TableIV. For a complete thermodynamic understanding, the enthalpy of micellization ($\Delta H^{\circ}_{m}$) has also been evaluated from the Vant Haff equation. (Eq. 2).

$$\Delta H^{\circ}_{m}=RT^{2}\,(d\ln(\mathrm{CMC})/dt) \qquad \ldots(2)$$

ln CMC was plotted against $T$ and the slope is equal to $d$ (ln (CMC)/$dT$). The standard entropy of micellization can then be calculated from Eqn. (3).

$$\Delta S^{\circ}_{m}=(\Delta H^{\circ}_{m}-\Delta G^{\circ}_{m})/T \qquad \ldots((3)$$

All the thermodynamic parameters are given in Table IV. The formation of the different micelle is energetically comparable. As expected, all the micellization processes end up with a considerable positive entropy change. The $\Delta H^{\circ}_{m} < T\Delta S^{\circ}_{m}$ results manifest the micellization process to be entropy controlled. At 308K, the entropy increase follows the order CTACl> CPB> CPC> BC> CTAB> CDEAB> TTAB> DTAB. The formation of micelles is connected with a large, negative change in $\Delta G^{\circ}_{m}$, i.e. the aggregation process is thermodynamically favoured and spontaneous.

Table IV shows that the enthalpies of micellization depend on the temperature. It is clear that at higher temperatures whole of the system becomes relatively more endothermic. Reports of the other workers also support this.

The entropy of micellization is very high, this type of entropy change is generally associated with phase change and one can assume micelles are a new phase. The positive entropy of micellization also indicates overall randomness in the systems due to release of structured water molecules around hydrocarbon chains. These values can also demonstrate the importance of hydrophobic interactions. It is assumed that the aggregation number and counterion binding of the micelle are not affected by temperature variation.

## Effect of counterions

The counterions are also important for the thermodynamics of micellization. The enthalpy of micellization is strongly dependent on the size of the halide counterion. Enthalpies of micellization are more endothermic for cationic surfactants with smaller counterions (CTAB-CTACl : CPB-CPC). This indicates that the influence of counterion is significant. According to Maa *et. al.*[19], counterions are unimportant for the thermodynamics of micellization.

The data in Table IV also show that $\Delta G^{\circ}_{m}$ decreases with increasing chain length of the hydrophobic moiety (DTAB, TTAB and CTAB). This increase per $CH_2$ group is expected due to hydrophobic Gibbs energies of transfer [20]. The change of the aggregation number with counterion should also be taken into account, unfortunately the aggregation numbers have not been determined.

## Solvent effect

It is well known that micellar properties of both cationic and anionic surfactants are significantly influenced by solvents [21-26]. The physicochemical properties of solvents, dielectric constant, hydrogen bonding ability, polarity, and cohesiveness parameters all play vital roles.

## Effects of dioxane

Herein we report the thermodynamics of micellization of CTAB in binary combination of water dioxane through the measurement of critical micelle concentrations employing the methods of conductance. The results are presented in Table II. For the binary mixture of dioxane and water, the CMC values first increase upto 10% and then decrease continuously. The features of the variation of CMC on the solvent compositions can not be accounted for mainly due to polarity effect. The CMC values increase as a function of temperature. Our observation can be explained in terms of the two interactions responsible for the micellization i.e. hydrophobic interactions and break-up of the water structure. On one hand the higher temperatures, enhance the disruption of the water structure, which on the other hand, diminish hydrophobic interactions.

In case of CTAB, dioxane water ternary systems, $\Delta G^{\circ}_{m}$ value decreases with the increase of concentration of dioxane, and for this system is more negative than the value determined for the formation of CTAB micelle in pure water (Table V). The enthalpy of micellization $\Delta H^{\circ}_{m}$ is more endothermic with respect to an increase in the concentration of dioxane. The entropy of

**Table II**—Critical micelle concentration of CTAB in various aquo-dioxane solution at different temperatures

| Solvents % (v/v) | CMC (m*M*) | | | |
|---|---|---|---|---|
| | 308K | 318 K | 328 K | 338 K |
| 0 | 1.30 | 1.20 | 1.10 | 1.00 |
| 10 | 2.40 | 2.20 | 1.20 | 0.80 |
| 20 | 1.71 | 1.00 | 0.99 | 0.63 |
| 30 | 1.50 | 1.00 | 0.80 | 0.60 |
| 40 | 1.30 | 0.90 | 0.70 | 0.40 |
| 50 | 1.20 | 0.80 | 0.60 | 0.31 |
| 60 | 1.10 | 0.70 | 0.60 | 0.29 |

**Table III**—Critical micelle concentration of CTAB in various co-solvents solution at different temperatures

| % Co-solvent | CMC ( mM) | | | |
|---|---|---|---|---|
| | 308 K | 318 K | 328 K | 338 K |
| Dioxane | 1.71 | 1.00 | 0.99 | 0.63 |
| DMSO | 1.90 | 1.40 | 1.20 | 1.00 |
| DMF | 2.20 | 1.39 | 1.00 | 1.00 |
| THF | 1.90 | 1.20 | 1.00 | 0.80 |
| $CH_3CN$ | 2.00 | 1.61 | 1.20 | 1.00 |
| MeOH | 1.70 | 1.40 | 1.20 | 0.80 |
| PrOH | 1.50 | 1.10 | 1.00 | 0.60 |

% of co-solvents = 20% (v/v)

**Table IV**—Thermodynamic quantities of micellization of surfactants at different temperatures

| Surfactants | $[\Delta G^{\circ}_{m}]$ KJmo l$^{-1}$ | | | | $[\Delta H^{\circ}_{m}]$ KJmo l$^{-1}$ | | | | $[\Delta S^{\circ}_{m}]$ JKmol | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 308 K | 318 K | 328 K | 338 K | 308 K | 318 K | 328 K | 338 K | 308 K | 318 K | 328 K | 338 |
| DTAB | 18.7 | 20.0 | 20.9 | 23.4 | 6.03 | 6.43 | 6.84 | 7.26 | 80.4 | 83.4 | 84.8 | 90.7 |
| TTAB | 22.6 | 25.5 | 26.6 | 28.5 | 2.50 | 2.67 | 2.84 | 3.01 | 81.5 | 88.7 | 89.7 | 93.3 |
| CTAB | 28.9 | 30.2 | 31.7 | 33.3 | 6.80 | 7.33 | 7.80 | 8.28 | 115.9 | 118.0 | 120.4 | 123.0 |
| CTACl | 27.3 | 28.6 | 30.7 | 33.3 | 18.3 | 19.6 | 20.8 | 22.1 | 148.2 | 151.6 | 157.7 | 163.9 |
| CDEAB | 27.8 | 30.5 | 31.8 | 33.8 | 5.13 | 5.40 | 5.82 | 6.18 | 107.1 | 113.2 | 114.6 | 118.2 |
| CPC | 28.4 | 31.8 | 33.6 | 36.6 | 14.8 | 15.8 | 16.8 | 17.9 | 140.3 | 149.9 | 153.7 | 160.3 |
| CPB | 26.4 | 29.5 | 32.6 | 34.2 | 9.07 | 9.67 | 10.3 | 10.9 | 115.2 | 123.3 | 130.6 | 133.4 |
| BC | 27.03 | 28.5 | 27.9 | 31.0 | 7.57 | 8.07 | 8.53 | 9.12 | 91.12 | 115.0 | 117.2 | 118.9 |

**Table V**—Thermodynamic quantities of micellization of CTAB in aquo-dioxane mixtures

| % Dioxane | $[\Delta G^{\circ}_{m}]$ KJmo l$^{-1}$ | | | | $[\Delta H^{\circ}_{m}]$ KJmo l$^{-1}$ | | | | $[\Delta S^{\circ}_{m}]$ JKmol | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 308 K | 318 K | 328 K | 338 K | 308 K | 318 K | 328 K | 338 K | 308 K | 318 K | 328 K | 338 |
| 0 | 28.2 | 30.2 | 31.7 | 33.3 | 6.80 | 7.33 | 7.80 | 8.28 | 115.9 | 118.0 | 120.4 | 123.0 |
| 10 | 27.9 | 29.2 | 33.2 | 36.2 | 30.8 | 32.8 | 34.9 | 37.1 | 190.0 | 195.8 | 207.1 | 216.6 |
| 20 | 29.6 | 33.2 | 34.3 | 37.6 | 23.7 | 25.2 | 36.8 | 28.5 | 173.3 | 183.9 | 186.9 | 286.5 |
| 30 | 30.5 | 32.9 | 35.6 | 38.1 | 24.1 | 25.7 | 27.4 | 29.1 | 171.6 | 184.4 | 192.2 | 199.1 |
| 40 | 31.6 | 34.5 | 36.8 | 40.8 | 29.8 | 31.8 | 23.8 | 35.9 | 199.6 | 208.5 | 115.5 | 221.3 |
| 50 | 32.5 | 36.6 | 38.2 | 42.9 | 34.2 | 36.4 | 38.8 | 41.2 | 216.8 | 229.4 | 135.5 | 249.1 |
| 60 | 33.1 | 36.5 | 38.4 | 43.4 | 35.7 | 37.5 | 39.8 | 42.5 | 223.2 | 235.2 | 136.6 | 254.3 |

micellization $\Delta S^{\circ}_{m}$ gradually increases. This implies that the positive free energy of micellization is principally that results of the entropy of terms of water CTAB-dioxane. This conclusion is in agreement with the general concept that micelle formation in aqueous solution is an entropy directed process and arises mainly from the break-up of the ordered water structure, even though the formation of aggregate by the surfactant molecules is entropy decreasing process.

## Effect of co-solvent

The comparison with micelle formation for CTAB in other aquo-solutions including co-solvents such as DMSO, DMF,THF, acetonitrile, methanol, *n*-propanal has been made (Table III). The effect of micellization of hexadecyltrimethyl ammonium bromide in different co-solvents (Table III) indicate that alcoholic solvents enhance the micelle formation while other retard it. This phenomena is due to hydrogen bounding and structure of water molecule with increase in temperature. The H-bonding of –OH group solvents is distructed, whereas in other solvents it is not possible.

Thermodynamic parameters, such as $\Delta G^{\circ}_{m}$, $\Delta H^{\circ}_{m}$, $\Delta S^{\circ}_{m}$ in different solvents were also determined. The experimental results indicate that micelle formation comparatively decreases with the rise in temperature, and solvents have

**Table VI**—Thermodynamic quantities of micellization of CTAB in different aquo-co-solvents mixtures

| Solvent (20%) | $[\Delta G^{\circ}_{m}]$ KJmo $l^{-1}$ | | | | $[\Delta H^{\circ}_{m}]$ KJmo $l^{-1}$ | | | | $[\Delta S^{\circ}_{m}]$ JKmol | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 308 K | 318 K | 328 K | 338 K | 308 K | 318 K | 328 K | 338 K | 308 K | 318 K | 328 K | 338 |
| Dioxane | 29.68 | 33.23 | 34.32 | 37.67 | 23.70 | 25.26 | 26.88 | 28.59 | 173.31 | 183.92 | 186.58 | 195.80 |
| DMSO | 28.64 | 30.96 | 32.70 | 34.92 | 18.05 | 19.24 | 20.47 | 21.74 | 151.50 | 157.8 | 162.10 | 167.60 |
| DMF | 27.25 | 30.18 | 32.74 | 34.83 | 27.04 | 28.82 | 30.67 | 32.57 | 176.20 | 182.50 | 193.30 | 199.40 |
| THF | 29.06 | 32.20 | 34.11 | 36.24 | 21.90 | 23.34 | 24.83 | 26.37 | 165.40 | 174.6 | 179.60 | 185.20 |
| Methanol | 29.70 | 31.59 | 33.37 | 36.40 | 19.02 | 20.28 | 21.59 | 22.91 | 158.10 | 163.1 | 167.50 | 175.40 |
| Acetonitrile | 30.00 | 32.40 | 34.82 | 37.58 | 18.66 | 19.90 | 21.17 | 22.48 | 157.90 | 164.4 | 170.70 | 177.60 |
| Propanol 2-01 | 30.80 | 34.38 | 36.09 | 39.80 | 22.43 | 23.91 | 25.43 | 27.01 | 172.8 | 183.9 | 187.50 | 197.60 |

enhancing effect on the formation of micelles of CTAB. This effect increases with increasing dioxane concentration. The effect of micellization and the observed changes in $\Delta G^{\circ}_{m}$, $\Delta H^{\circ}_{m}$, and $\Delta S^{\circ}_{m}$ can be explained in terms of interaction, such as hydrogen bonding between water and solvents resulting in the increase of hydrophobic forces in the ternary system (Table VI)

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