

Micellar Properties of Alkyltrimethyl Ammonium Bromide in Aquo-organic Solvent Media

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Abstract

The thermodynamics of micellization and other micellar properties of cationic alkyl (C_{12} , C_{14} and C_{16}) trimethylammonium bromide surfactants in presence of water-dimethylformamide (5-20 % v/v) binary mixtures over a temperature range of 298-318 K have been studied conductometrically. On the basis of the results, the critical micelle concentration, degree of micellar ionization and thermodynamic parameters, free energy, enthalpy and entropy (ΔG_m^0 , ΔH_m^0 and ΔS_m^0) of micellization have been determined. The increase of critical micelle concentration with solvent mixtures has been discussed on the basis of water structure, solvent properties and hydrophobic interaction.

Keywords: Thermodynamics, surfactants, micellization, solvent effect.

Introduction

Surfactant molecules when dissolved in water above a certain concentration, referred to as critical micellar concentration (*cmc*), self-aggregate into supramolecular structure. The simplest aggregate of these surfactant molecules is called a micelle and the dispersion of these aggregates in aqueous solution is referred to as a micellar solution¹. The investigation of interfacial and thermodynamic properties of surfactants in solution, both in the presence and in the absence of additives, can provide extensive information about solute-solute and solute-solvent interaction of the surfactant in solution². The interfacial and micelle properties of surfactant solution are governed by a delicate balance of solvophobic and solvophilic interaction. These characteristics can be modified in two ways: (i) through specific interaction with the surfactant molecules and (ii) by changing the nature of the solvent. Such studies on the effects of cosolvents on the aggregation and other physicochemical properties of surfactants are of fundamental and industrial

interest³. Much effort has been devoted in exploring the nature of micellization and surfactant behavior in polar organic solvents and solvent mixtures⁴⁻¹⁷. The micellization process of various ionic and non-ionic surfactants in polar organic solvents and aqueous organic mixed systems has been extensively investigated¹⁸⁻²².

Survey of available literature reveals that no serious attempt has been made to study the micellization phenomenon of alkyltrimethyl ammonium bromide surfactant in polar and non-aqueous solvent. Here in we report the critical micellar concentration, degree of micellar ionization and other thermodynamic parameters, free energy, enthalpy and entropy of micellization in binary mixtures of water-dimethylformamide (v/v).

Material and Methods

The surfactants cetyltrimethylammonium bromide tetradecyltrimethylammonium bromide and dodecyltrimethylammonium bromide were obtained from S. D. fine chemicals (Mumbai-India). The

solvent dimethylformamide was obtained from Qualigens and use without further purification. All the solutions were prepared in triply distilled water.

Conductometric measurements were carried out using a Systronic microprocessor based conductivity meter (Type 306). The conductivity cell was calibrated with KCl solutions in appropriate concentration range. A concentrated surfactant solution was progressively added to 25 ml of water or desired aquo-organic solvent mixture in a thermostated container (temperature accuracy ± 0.1) using a Qualigens variables volume micropipette. After ensuring thorough mixing and temperature equilibrium of 298-318 K, the specific conductance (κ) was measured. The break point was observed by plotting specific conductivity versus concentration and point was assumed to be the *cmc* of surfactants.

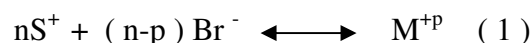
Results and Discussion

The critical micelle concentration, *cmc* of the surfactants DTAB, TTAB and CTAB under condition has been determined from the plots of specific conductivity, κ , versus surfactant concentration. The conductivity is linearly correlated to the surfactant concentration in both pre-micellar and post-micellar regions, having a slope in the pre-micellar region. The intersection point between the two straight lines gives the *cmc* and the degree of ionization α , is calculated from the ratio of the slope of κ versus surfactant concentration above and below the *cmc*. The *cmc* values and micellar ionization degree, α , of the cationic surfactants in binary aqueous-solvent solutions are also listed in table 1. For all the surfactants studied an increase in the amount of solvent present in the solution results in an increase in the critical micelle concentration and an increase in the degree of ionization with respect to water. The behavior can be interpreted in term of solvent interpretation with water and its possible influence on solvophobic forces operating for micellization. Hydrophobic interactions and electrostatic repulsion are important factors for micellization. The dielectric constant decreases with increasing % (v/v) solvent. This decrease in the

dielectric constant is expected to cause an increase in the electrostatic repulsions between the cationic head groups at the micellar surface and decrease hydrophobic interactions between the hydrocarbon tails. As a result, the *cmc* and α increases with increasing the amount of organic solvent

The delay in micellization in case of DMF can be explained by taking into consideration the increased structuring of the H₂O-DMF liquid system. DMF is known to form stoichiometric hydrates with water of the type DMF.H₂O. The formation of hydrate substantially restricts the motion of the surfactant molecules and reduces hydrophobic interactions with a concomitant increase in *cmc*. The dielectric constant of DMF is much smaller than that of water. However, with arise in volume percentage of DMF the dielectric constant, the ionic interaction at the micellar surface increases. Also, these interactions decrease with an increase in volume percent of DMF in the micellar medium and hence the *cmc* value increases²³⁻²⁴.

Therodynamics of Micellization: The dependence of *cmc* upon the temperature was used to evaluate the standard thermodynamic parameters of micellization for surfactant solvent systems. The change in the *cmc* value with temperature is generally analyzed in terms of the phase separation or equilibrium model for micelle formation²⁵. The micellization takes place where the energy as result of association of hydrocarbon chain of the monomer is sufficient to overcome the electrical repulsion between the ionic head group and decrease in entropy accompanying the aggregation. Therefore, in the study the increase in temperature results in an increase in *cmc* values because the kinetic energy of monomer has been raised²⁶⁻²⁷. According to this model, the equilibrium between surfactant and micelles can be represented by eq. 1



Where S⁺ represents the cationic surfactants and M represents the micelle. The standard free energy of micelle formation per monomer unit is

$$\Delta G_m^0 / RT = -1/n \ln C_m^{+p} + C_s^+ + (1-p/n) \ln C_{Br}^- \quad (2)$$

Since n is larger (50-100) the C_m^{+p} is smaller and is sensitive to larger error in the estimated C_m^{+p} , both C_S^+ and C_{Br^-} can be replaced by the cmc (expressed in mole fraction). In the second and third terms in equation 2 gives

$$\Delta G_m^0 = (2 - \alpha) RT \ln X_{cmc} \quad (3)$$

Where R is the gas constant, T is the absolute temperature, α is the degree of ionization and X_{cmc} is the cmc value on mole fraction scale. Values of ΔG_m^0 are determined by eq. 3.

The enthalpies of micellization were calculated using equation 4.

$$\Delta H_m^0 = - (2 - \alpha) RT^2 (d \ln X_{cmc} / dT) \quad (4)$$

Therefore, if the dependence of cmc values on temperature is known, $\ln X_{cmc}$ versus temperature can be plotted. The slope can be found at each temperature. A typical plot for CTAB in 10 % (v/v) DMSO is presented in figure 1. The entropies of micellization were calculated from equation 5.

$$\Delta S_m^0 = \Delta H_m^0 - \Delta G_m^0 / T \quad (5)$$

The thermodynamics of micellization were calculated for the alkyltrimethylammonium bromides surfactant in the presence of 5% (v/v), 10% (v/v) and 20% v/v water-dimethyl formamide mixtures at temperature range 298-318 K. The values obtained for these parameters are given in tables-1. The error in the free energy and enthalpy values is $\pm 0.5 \text{ k J mol}^{-1}$, while the error in the entropy values is $\pm 5 \text{ J K}^{-1} \text{ mole}^{-1}$. It is evident that the free energies of micellization decrease with increasing length of hydrocarbon chain. As previously mentioned, the free energies of micellization give an indication of the readiness with which the micelles form. It was found that the cmc values decrease with increasing chain length and the free energies of micellization follow the same trend. This indicates an increased hydrophobic effect for the longer chain surfactants.

From table-1 it can be seen that the cmc values increase with increasing volume percent of dimethylformamide. As the amount of DMF in the media increases, the structure of the water molecules around the hydrophobic chains gets destructed resulting in the increase of cmc . The free energies of micellization are seen to become more negative with increasing temperature in pure water and also in the presence of additives for all of the surfactants. This can be explained in terms of the change in magnitude of the logarithm of the cmc is being more than compensated by the RT term in equation 3.

It can be seen from table 2-4 that the enthalpies of micellization were found to become more negative with increasing temperature for each surfactant in each solvent. The enthalpies calculated from equation 4 may differ from the values determined calorimetrically. The equation employed to determine free energies is only applicable if the aggregation numbers are large and activities are replaced by concentrations as the solutions are dilute. Therefore the thermodynamics values should be viewed as approximate; however generalizations can still be drawn from the data. The data indicate that the micellization is favored mainly by entropy at low temperature.

Conclusion

The cmc , α value and the thermodynamic parameters of the process of micellization have been evaluated for alkyl (C_{12} , C_{14} , and C_{16}) trimethylammonium bromide systems. It was observed that both the cmc and α value were dependent upon the (v/v %) of solvent and temperature and the micellization tendency of cationic surfactant decreases in the presence of solvents. The free energies of micellization (ΔG_m^0) are seen to become more negative with increasing temperature in pure water and also in the presence of additives for all of the surfactants. This suggests that micelle formation becomes less spontaneous with increasing amount of solvents. It was observed that the micellization is favored in general by entropy and enthalpy at higher temperatures, whereas it is favored mainly by entropy at low temperatures.

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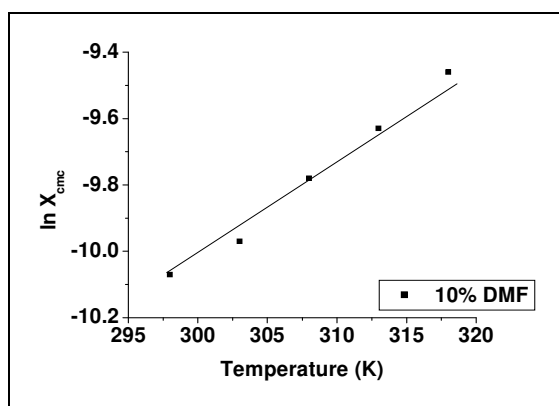


Figure- 1: Variation of $\ln X_{cmc}$ of CTAB in 10% (v/v) Dimethylformamide with temperature

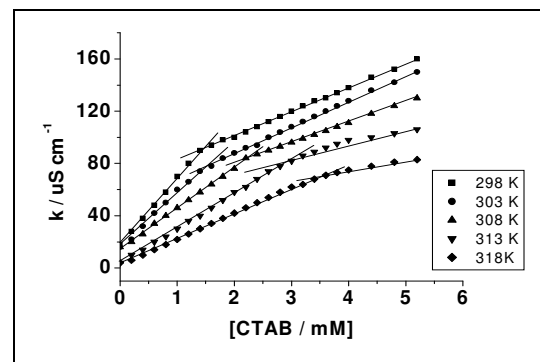


Figure -2: Plots of Specific conductance (κ) vs. [CTAB] at different temperatures in presence of 5% (v/v) water- Dimethylformamide

Table-1: *cmc* and degree of dissociation of counter ions (α) values of the Alkyltrimethylammonium bromides, in the presence of dimethyl formamide .

Surfactant	Temperature (K)	<i>cmc</i> in 5% (v/v) DMF mM	α	<i>cmc</i> in 10% (v/v) DMF mM	α	<i>cmc</i> in 20% (v/v) DMF mM	α
DTAB	298	15.8	0.45	22.2	0.46	--	--
	303	16.0	0.50	22.3	0.53	--	--
	308	16.8	0.55	23.2	0.60	--	--
	313	17.4	0.61	24.5	0.65	--	--
	318	18.5	0.64	25.0	0.67	--	--
TTAB	298	4.85	0.37	6.37	0.42	9.63	0.45
	303	4.96	0.43	6.78	0.48	9.92	0.52
	308	5.32	0.48	7.42	0.53	10.2	0.58
	313	5.97	0.50	8.12	0.60	10.7	0.65
	318	6.34	0.55	8.83	0.64	11.3	0.73
CTAB	298	1.43	0.36	2.38	0.38	4.00	0.40
	303	1.51	0.37	2.56	0.40	4.20	0.43
	308	2.21	0.40	3.12	0.45	4.40	0.46
	313	2.87	0.45	3.65	0.48	5.00	0.48
	318	3.54	0.55	4.31	0.53	6.02	0.55

Table-2: Thermodynamic Parameters of Alkyltrimethylammonium bromides in 5% (v/v) Dimethyl formamide

Surfactant	Temperature	ΔG_m^0 ($kJ mol^{-1}$)	ΔH_m^0 ($kJ mol^{-1}$)	ΔS_m^0 ($JK^{-1} mol^{-1}$)
DTAB	298	- 31.3	-9.1	74.4
	303	- 30.8	- 9.5	70.4
	308	- 30.0	-9.1	67.7
	313	- 29.1	-9.0	64.2
	318	-28.8	- 9.0	61.8
TTAB	298	- 37.7	- 31.2	21.8
	303	- 36.8	- 31.1	18.8
	308	- 36.0	- 31.1	15.9
	313	-35.6	-31.7	12.4
	318	- 34.7	- 31.8	9.4
CTAB	298	- 43.0	-54.4	38.4
	303	- 43.1	-55.9	42.3
	308	- 41.5	-56.7	49.1
	313	- 39.8	-56.8	54.1
	318	-37.5	-54.8	54.0

Table-3: Thermodynamic Parameters of Alkyltrimethylammonium bromides in 10% (v/v) Dimethyl formamide

Surfactant	Temperature	$\Delta G_m^0 (kJ mol^{-1})$	$\Delta H_m^0 (kJ mol^{-1})$	$\Delta S_m^0 (JK^{-1} mol^{-1})$
DTAB	298	- 29.8	-6.8	77.1
	303	- 28.8	- 6.7	73.1
	308	-27.6	- 6.6	69.1
	313	- 26.9	-6.5	64.8
	318	- 26.4	-6.7	62.8
TTAB	298	- 35.6	- 18.6	57.0
	303	- 34.5	- 18.5	52.8
	308	- 33.6	- 18.5	49.0
	313	- 32.3	- 18.2	45.0
	318	- 31.6	-18.2	41.8
CTAB	298	- 40.4	- 29.5	35.2
	303	- 40.1	-30.5	32.0
	308	- 39.4	-30.6	28.8
	313	-38.0	-30.9	22.8
	318	-36.7	-30.8	18.4

Table-4: Thermodynamic Parameters of Alkyltrimethylammonium bromides in 20% (v/v) Dimethyl formamide

Surfactant	Temperature	$\Delta G_m^0 (kJ mol^{-1})$	$\Delta H_m^0 (kJ mol^{-1})$	$\Delta S_m^0 (JK^{-1} mol^{-1})$
TTAB	298	-33.5	-11.4	74.1
	303	-32.1	-11.3	68.6
	308	-30.7	-11.1	63.3
	313	-30.0	-10.1	63.5
	318	-28.5	-10.6	56.2
CTAB	298	-37.8	-21.2	55.7
	303	-37.7	-21.5	53.4
	308	-37.2	-21.8	50.0
	313	-36.6	-22.2	46.0
	318	-38.0	-21.9	50.7

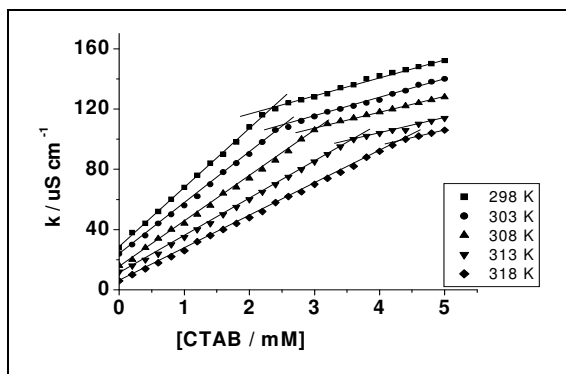


Figure-3: Plots of Specific conductance (κ) vs. [CTAB] at different temperatures in presence of 10% (v/v) water- Dimethylformamide

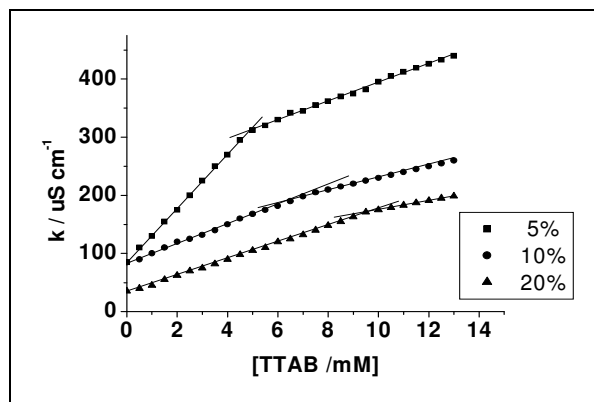


Figure -5: Plots of Specific conductance (κ) vs. [TTAB] in 5%, 10% and 20% (v/v) water- Dimethylformamide binary solvent at 298 K

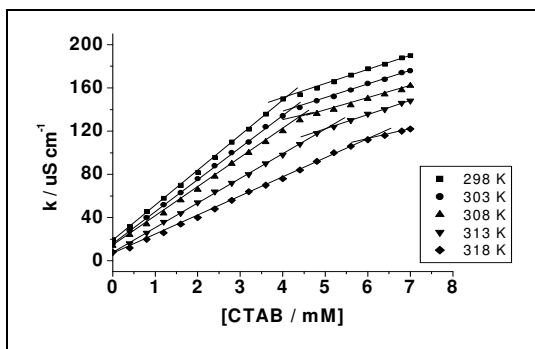


Figure - 4: Plots of Specific conductance (κ) vs. [CTAB] at different temperatures in presence of 20% (v/v) water- Dimethylformamide

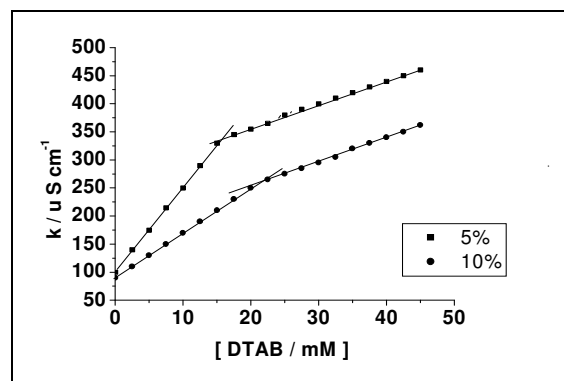


Figure - 6: Plots of Specific conductance (κ) vs. [DTAB] in 5%, 10% (v/v) water- Dimethylformamide binary solvent at 298 K