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Spectroscopic and surface tension study of aqueous solutions of tetraethylammonium bromide in the presence of crown ether

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ABSTRACT

Spectroscopic and surface tension measurements have been carried out to study the micellar behavior of aqueous solutions of Tetraethylammonium bromide in absence and presence of crown ether. The molar absorptivity coefficient 'ε' has been determined for the aqueous micellar solutions both in absence and presence of crown ether. Binding constant, K has been used to analyze the stability of the inclusion complexes. The values of critical micelle concentration, maximum surface excess concentration and minimum area per molecule of the surfactant have been evaluated. Thermodynamics of the systems was discussed in terms of the change in standard free energy of micellization and standard Gibb's energy change of adsorption. The resulting parameters allow the observation of concomitant reorganizations occurring in the system. © 2011 Trade Science Inc. - INDIA

KEYWORDS

Tetraethylammonium
bromide;
Crown ether;
UV-Visible
spectrophotometry;
Molar absorptivity
coefficient;
Surface tension;
Maximum surface excess
concentration.

INTRODUCTION

Surfactants have micellar properties, which are affected by addition of small amount of electrolytes, non-polar and polar organic compounds^[1]. Although the solubilization of additives in micelles makes the micellar system more complicated than the binary system, it provides an additional opportunity to explore micelle structure and micellar solution properties in terms of the interaction between the micelles and the additives. Crown ethers are heterocyclic chemical compounds that consist of a ring containing several ether groups. Crown ethers and related macrocycles are known to mimic some parts of biological molecular recognition and to mediate subsequent chemical processes. These mac-

rocyclic compounds have also been found to interact with amphiphilic molecules, like ionic surfactants. While dealing with the macrocycle-surfactant solution, a certain type of association can be observed between the micelles and the macrocyclic cavity in water. The nature of such association results in the formation of inclusion complexes^[1-5].

The objective of the present study is to study the encapsulation processes of cationic Tetraethylammonium bromide (quaternary ammonium compound) by 15-crown-5-ether (CE) and its effect in the micellization process of the surfactant itself. Spectroscopic and surface tension measurements were done to predict the thermodynamic parameters of micellization/adsorption and to understand the type of interactions existing in the

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system respectively. In all, the influence of the presence of the inclusion complex on the micellization process of the surfactant has been focused in detail.

EXPERIMENTAL

Materials

Tetraethylammonium bromide (TBR) (Purity >99%, water content <1%) obtained from Merck was recrystallized with chloroform-ether mixture and carefully dried in a hot air oven to constant weight. The Crown ether, 15-crown-5 (CE) from Fluka (Purity >99%) was used as received. The water used to prepare the aqueous solutions was triply distilled with the conductance <3.0 μS .

Methods

The solutions were prepared by weight using an electronic balance with an accuracy of $\pm 1 \times 10^{-4}$ g. For binary S/W system and the ternary S/CE/W systems, the concentration of the surfactant was varied from 0.01-0.3M and CE concentration was varied from 1-3mM. In each measurement concentration of crown ether was kept constant.

The UV-visible spectra were recorded with JASCO V-530 spectrophotometer using quartz cells. Surface tension measurements were done at $15.0 \pm 0.002^\circ\text{C}$ using Kruss processor tensiometer with an accuracy of 0.01 mNm^{-1} .

RESULTS AND DISCUSSION

A solute can arrange itself in the micelle in different ways: it may be completely incorporated in the hydrophobic core or may penetrate up to a certain depth; it can be adsorbed on the micellar surface or can selectively interact with the polar or non polar part of the surfactant molecules depending upon the nature of its substituents. In order to have deeper insight in our micellar systems, spectroscopic and surface tension measurements were carried out at constant temperature.

UV-vis spectroscopic measurements

Spectroscopic analysis of inclusion complexes of 15-crown-5-ether (CE) with cationic surfactant Tetraethylammonium bromide (TBR) has been investigated

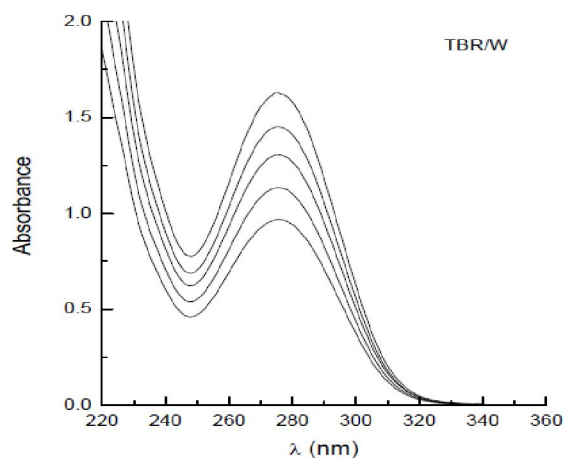


Figure 1 : UV-visible spectra of binary TBR/W system

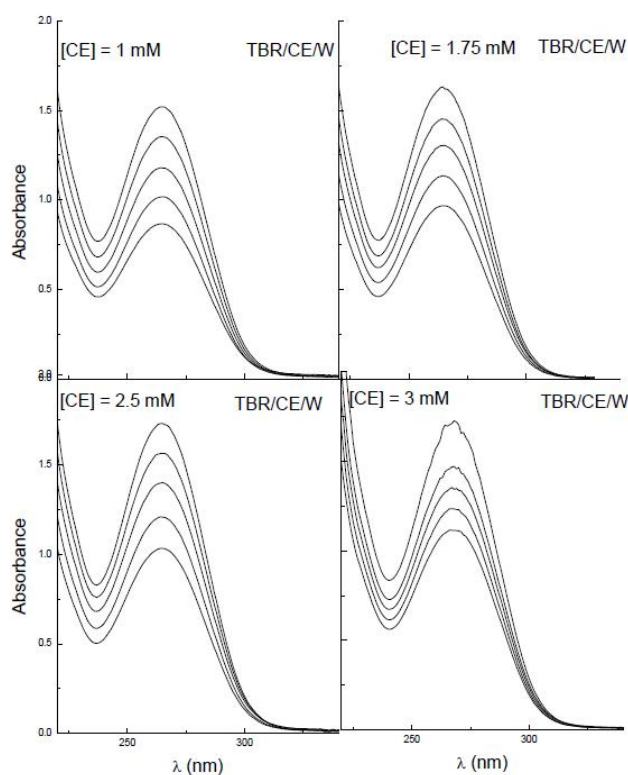


Figure 2 : UV-visible spectra of ternary TBR/CE/W systems

as a function of concentration of surfactants and CE. UV/visible spectra for the aqueous micellar systems show one characteristic peak at 245 nm both in the absence and in the presence of CE. The values of absorbance at $\lambda_{245 \text{ nm}}$ were fitted linearly as a function of surfactant concentration. The data obeys Beer-Lambert's law. The molar absorptivity coefficient ' ϵ ' for all the systems, was estimated from absorbance vs. conc. plots and the values are tabulated in TABLE 1. It is clearly seen that the molar absorptivities of the

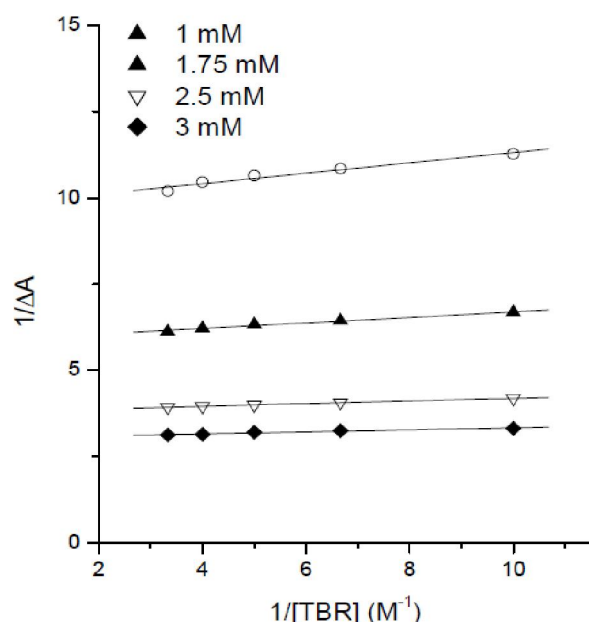


Figure 3 : Benesi-Hildebrand plots at different concentrations of CE

TABLE 1 : Estimated molar absorptivity coefficients and binding constants

[CE] (mM) (M)	$\epsilon(\text{M}^{-1} \text{cm}^{-1})$	$K(\text{M}^{-1})$
0	0.33	-
1	0.38	104.67
1.75	0.41	97.52
2.5	0.44	72.65
3	0.47	65.17

uncomplexed and complexed TBR differed at the same wavelength. It shows the increase in the magnitude of molar absorptivity coefficient “ ϵ ” in TBR\CE\W systems. This indicates more absorbance of TBR micelles due to lesser interaction with crown ether. It seems that there is onset of hydrophobic interactions as CE is added to the aqueous TBR micellar systems. Further increase in values with increase in concentration of CE may be due to the weak encapsulation effect of CE for TBR molecules.

Binding constant, K for the ternary systems has been calculated by using Benesi-Hildebrand equation^[6]:

$$\frac{1}{\Delta A} = \frac{1}{[S] \times K \Delta \epsilon} \times \frac{1}{[CE]} + \frac{1}{[S] \times \Delta \epsilon} \quad (1)$$

where, ΔA = change in absorbance, $[CE]$ = concentration of crown ether in moles/litre, $[S]$ = concentration of surfactant in moles/litre and $\Delta \epsilon$ = change in molar absorptivity coefficient.

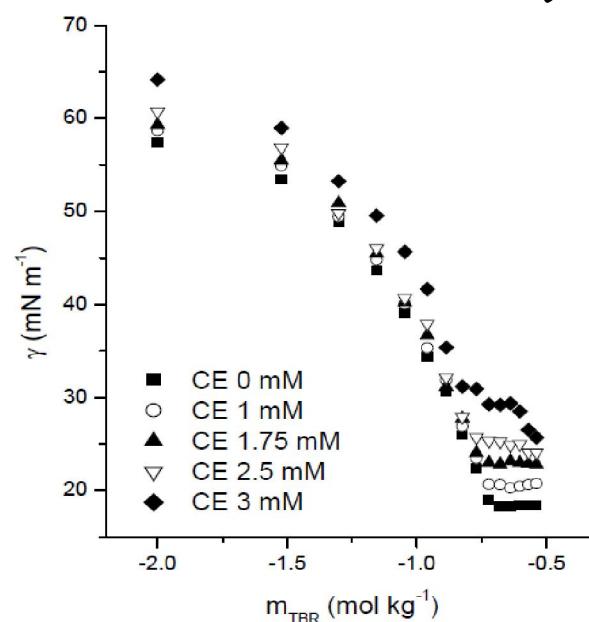


Figure 4 : Surface tension plots at different concentrations of CE

TABLE 2 : Thermodynamic parameters of the micellization/adsorption

M_{CE} (mM)	cmc (mol kg ⁻¹)	ΔG_m° (kJ mol ⁻¹)	$\Gamma_{max} \times 10^{10}$ (mol cm ⁻²)	$A_{min} \times 10^2$ (nm ²)	π_{cmc} (mN m ⁻¹)	ΔG_{ad}° (kJ mol ⁻¹)
0	0.187	-8.03	2.81	58.97	40.41	-14.36
1	0.174	-8.38	2.82	58.98	40.9	-14.53
1.75	0.163	-8.69	2.80	59.40	39.48	-14.12
2.5	0.155	-8.93	2.68	62.06	39.12	-14.62
3	0.149	-9.12	2.45	67.69	35.02	-14.28

It can be seen that increase in concentration of CE causes a decrease in the binding of the surfactants over the measured concentration range of the CE (Figure 3). This may be attributed to the increase of steric interactions. The above observations confirm the interaction between surfactant and CE so as to affect the micellization process. This aspect has been investigated using the physico-chemical measurements for the studied systems.

Surface/interfacial tension studies

The plots of surface tension (γ) vs. $\log m_{SDS}$ of aqueous solutions of the studied systems at 15°C are shown in figure 4. It was found that the presence of CE in SDS/W systems can depress the surface tension. The cmc values were obtained through a conventional plot of the surface/interfacial tension versus the surfactant concentration. The cmc concentration corresponds to the point where the surfactant first shows the lowest

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surface/interfacial tension. The surface/interfacial tension remains relatively constant after this point^[7-17]. As the surfactant concentration increases, surface/interfacial tension decreases until the surfactant cmc value is reached and remains relatively constant there afterwards. There is a decrease in cmc values as the concentration of CE is increased. This can be inferred that addition of CE is playing an important role in the micellisation process. From the surface tension plots, the maximum surface excess concentration, Γ_{\max} , and from the maximum adsorption, the minimum area per molecule, A_{\min} , were computed using the following equations^[11-12]:

$$\Gamma_{\max} = -\frac{1}{nRT} \left(\frac{\partial \gamma}{\partial \ln C} \right)_T$$

$$A_{\min} = 1/N \cdot \Gamma_{\max} \quad (2)$$

where R is the gas constant, N is Avogadro's number and C is the concentration of the surfactant in solution.

A decrease in Γ_{\max} values (TABLE 2) in the presence of CE may be due to the fact that addition of these macrocycles causes a partial displacement of surfactant molecules from the air-liquid interface to the bulk phase. A_{\min} increases both with the increase with the increase in concentration of CE in the surfactant solution (TABLE 2). This behaviour can be explained in terms of the enhanced compatibility of surfactant with the solvent in the presence of CE, thereby, causing a shift of surfactant molecules from air-liquid interface to the bulk phase. Surface pressure at CMC (π_{cmc}), an index of surface tension reduction at CMC, has been calculated using the equation^[11,12]:

$$\pi_{\text{cmc}} = \gamma_0 - \gamma_{\text{cmc}} \quad (3)$$

where γ_0 = surface tension of water and γ_{cmc} = surface tension of surfactant solution at CMC. π_{cmc} values (TABLE 2) show marginal decrease with increase in concentration of CE in the surfactant solution.

The standard Gibb's energy change of micellisation (ΔG_m°), has been calculated using the equations^[13]:

$$\Delta G_m^\circ = nRT \ln X \quad (4)$$

where X is the surfactant mole fraction at CMC. The ΔG_m° values are found to be negative indicating the spontaneity of micellization process in aqueous system (TABLE 2).

The standard Gibb's energy change of adsorption

($\Delta G_{\text{ad}}^\circ$), has been calculated using the equations^[13]:

$$\Delta G_{\text{ad}}^\circ = \Delta G_m^\circ - N\pi_{\text{cmc}} \cdot A_{\min} \quad (5)$$

The lower ΔG_a° values as compared to ΔG_m° indicates that adsorption of the surfactant molecules at the air-liquid interface is preferred over the micellization (TABLE 2).

CONCLUSION

The purpose of studying the additive effect of CE in surfactant/W mixture was to check the influence of CE on the micellization of TBR in the ternary mixtures. Addition of CE leads to reinforcement of the water structure through increased network of intermolecular interactions. Strengthening of the water structure forces the surfactant molecules to micellise at lower concentration and cmc is lowered. Surface tension studies reveal that the addition of CE causes a shift of surfactant molecules from the interface to the bulk of the solution. Thermodynamic parameters further support for the spontaneity of all the systems studied.

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