Spectroscopic analysis of crown ether – surfactant inclusion complexes in aqueous media

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ABSTRACT

Inclusion complexes of 15-crown-5-ether (CE) with two different surfactants, Sodium dodecyl sulphate (SDS) and Cetyl trimethyl ammonium bromide (CTAB) have been studied in aqueous solution spectroscopically. The molar absorptivity coefficient 'ε' has been determined for the aqueous micellar solutions both in absence and presence of crown ether. The 'ε' varies in the order CTAB/ W 〉 CTAB/ CE/W 〉 SDS/W 〉 SDS/CE/W. An increase in intensity of absorption of surfactants was observed with the increase in the concentration of crown ether. Binding constant, K has been used to analyse the stability of the inclusion complexes. Interaction of crown ether with Sodium dodecyl sulphate has been found to be more favorable as compared to Cetyl trimethyl ammonium bromide.

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INTRODUCTION

Surfactants place a special role in modern day to day life and technological applications. The properties of surfactants solutions largely depend upon the nature and amount of additives. 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[1-12].

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. Among the various properties of crown ethers, their unique chemical architecture plays a prominent role and opens the way to practical design of host molecules for selective complexation of various metal ions. However the rational design of new formulations requires a good knowledge of the encapsulation process. Several investigations based on crown ethers in micellar systems have been reported[13-22].

Structural information, such as the stoichiometry and the geometry of the complex, and thermodynamic information of binding, are necessary to draw a complete picture of the driving forces governing the crown ether-surfactant interactions. Keeping in view of the importance of complexation of crown ethers with surfactants, it was planned to investigate the association of 15-crown-5-ether (CE) with two different surfactants, Sodium dodecyl sulphate (SDS) and Cetyl trimethyl ammonium bromide (CTAB) in aqueous media with the

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help of UV/ visible spectroscopic technique.

EXPERIMENTAL

Materials

15-crown-5ether (CE) and Sodium dodecyl sulfate (SDS) having purity greater than 98% were purchased from Merck and Cetyltrimetyl ammonium bromide (CTAB) having purity greater than 98% was purchased from Fluka. All the chemicals were of analytical grade and were used without further purification. Water used for the preparation of samples was deionized and triply distilled (conductivity lower than 3μS).

Methods

The UV/Visible spectra were recorded with SHIMADJU UV-160 spectrophotometer using quartz cells having path length of 1cm each. For binary SDS/W system and the ternary S/ CE/ W systems, the concentration of the surfactant was varied from 3-15mM and CE concentration was varied from 1-10mM. In each measurement concentration of crown ether was kept constant.

RESULTS AND DISCUSSION

Spectroscopic analysis of inclusion complexes of 15-crown-5-ether (CE) with two different surfactants, Sodium dodecyl sulphate (SDS) and Cetyl trimethyl ammonium bromide (CTAB) has been investigated as a function of concentration of surfactants and CE. Figure 1 shows UV/visible spectra in the absence of CE

with one characteristic peak at 260 nm both for the aqueous micellar systems of SDS and CTAB. UV/visible spectra in the presence of CE with one characteristic peak at 260 nm both for the aqueous micellar systems of SDS and CTAB has been plotted in Figure 2. The values of absorbance at λ 260 nm were fitted linearly as a function of surfactant concentration (Figure 3). 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.

There is a decrease in the magnitude of molar absorptivity coefficient 'ϵ' in all ternary SDS /CE/W systems with increase of concentration of CE. This indicates less absorbance of SDS micelles due to its interaction with CE moities. However, there is an increase in the magnitude of molar absorptivity coefficient 'ϵ' in all ternary CTAB /CE/W systems with increase of concentration of CE. This indicates more absorbance of CTAB micelles due to its lesser interaction with CE moities. The results indicate a curve showing a diminution in the intensity of absorbance at 260 nm with increasing concentration of CE in all the cases. The molar absorptivities of the complex and surfactant differed at the same wavelength. This phenomenon may be assigned to the possibility of association between CE and surfactants. This can be visualized in a way that in the solution the surfactant molecule is interacting with CE molecule by orienting its hydrophillic groups towards the cavity of the CE and starts moving inside the cavity, which causes decrease in the surfactant concentration in the bulk solution and hence decrease in intensity of absorbance.
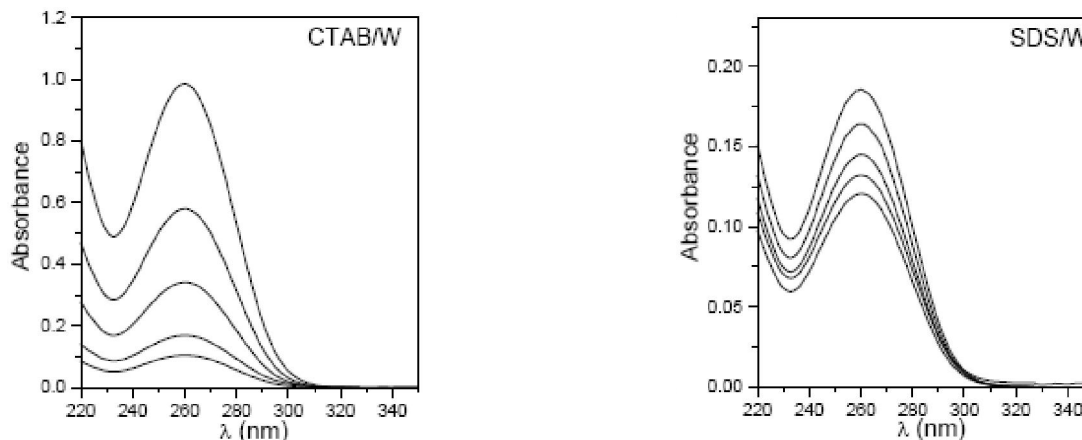

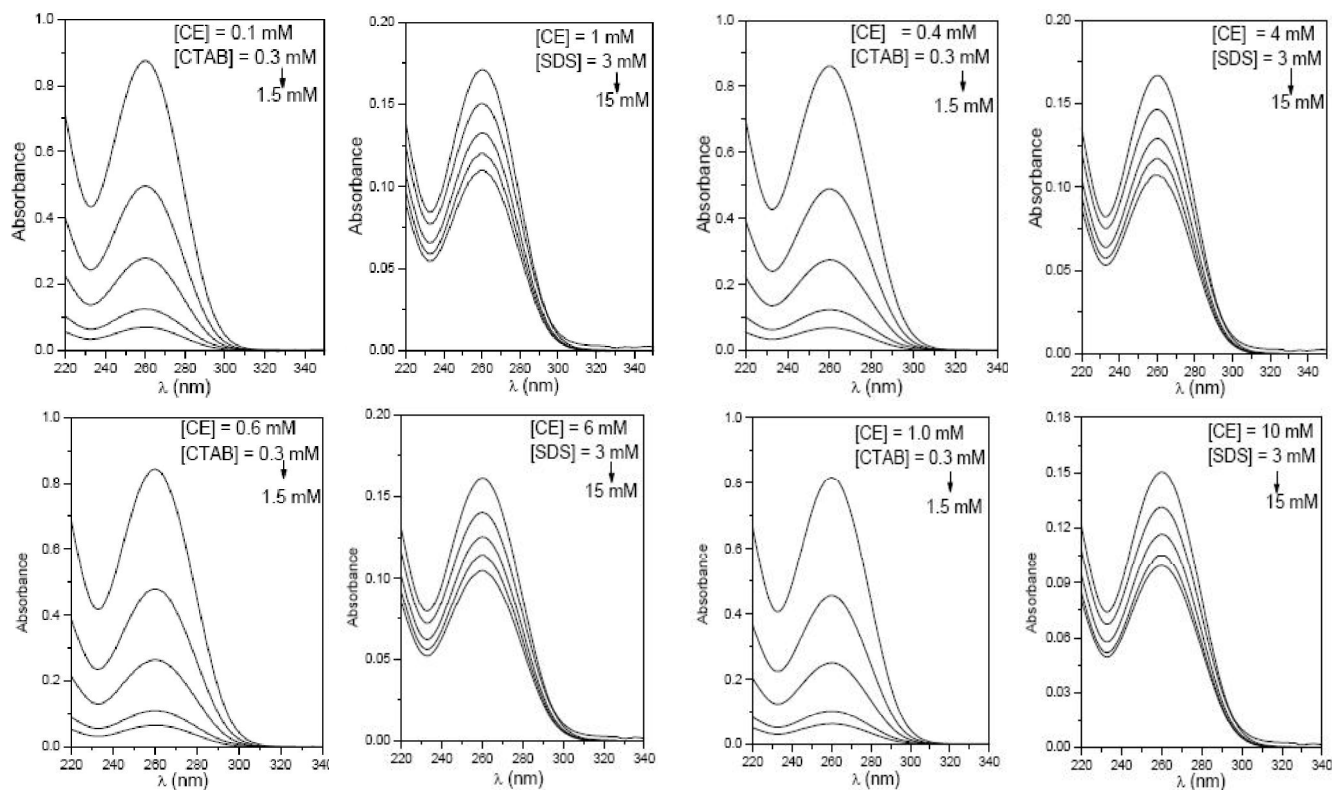**Figure 1 : UV-visible spectra of binary systems**

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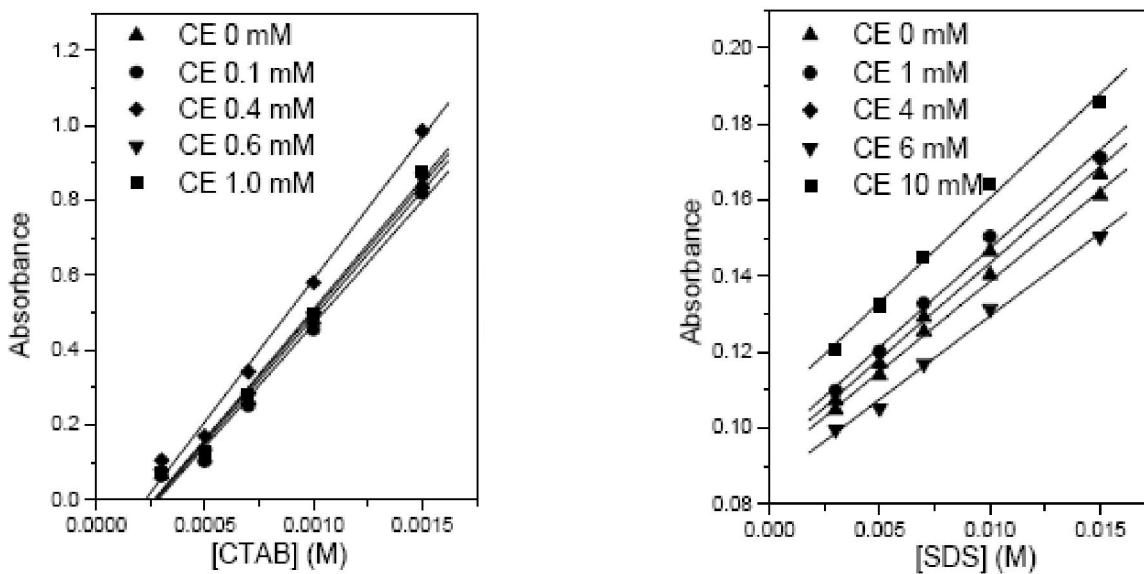**Figure 2 : UV-visible spectra of ternary systems**

Figure 3 : Lambert-Beer linear plots for aqueous solution of surfactants at different concentration in absence and presence of CE.

UV-Visible absorption spectroscopy is a commonly used technique for the determination of equilibrium constants, particularly in biochemical applications. The change in absorbance with concentration of S will be used to calculate the equilibrium constant for binding. Consider the following equilibrium:
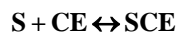
$$S + CE \leftrightarrow SCE$$

The equilibrium constant for this reaction is:
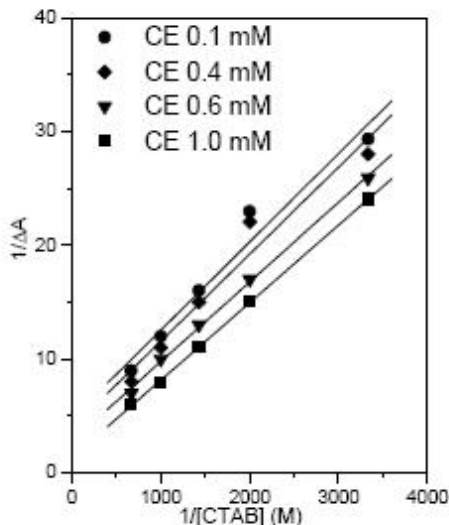
$$K = \frac{[SCE]}{[S][CE]}$$

Where, CE is uncomplexed crown ether and SCE is the crown ether – surfactant complex. The values of molar absorptivities have further been analyzed to calculate the binding constant of the association between

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surfactant and CE using the following equation[23,24]:

$$\frac{1}{\Delta A} = \frac{1}{[S]*K\Delta\varepsilon} * \frac{1}{[CE]} + \frac{1}{[S]*\Delta\varepsilon}$$

Where, A = change in absorbance, [CE] = concentra-

tion of crown ether in moles/litre, [S] = concentration of surfactant in moles/litre and $\Delta\varepsilon$ = change in molar absorptivity coefficient

Figure 4 shows the Benesi-Hildebrand plots between 1/ΔA and 1/[S]. The stability constant K was
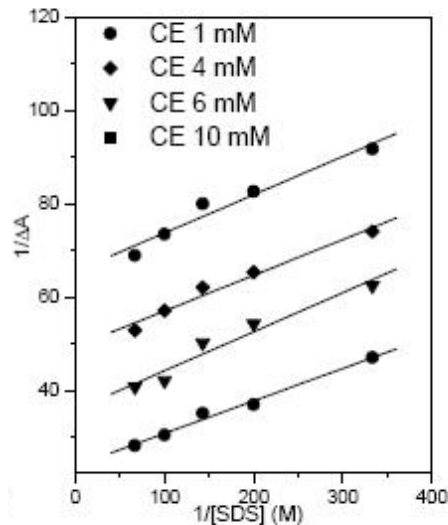

Figure 4 : Benesi-Hildebrand plots

calculated from the intercept/slope ratio for each system and are reported in TABLE 1. The estimated binding constant K value for SDS\CE\W system is larger as compared to a value for CTAB\ CE\W system. The higher value of K in case of SDS confirms that the association between CE and SDS is more favorable than CE and CTAB interactions.

TABLE 1 : Estimated molar absorptivity coefficients and binding constants

[CE] (mM)	ε ($M^{-1}cm^{-1}$)	K (M^{-1})	[CE] (mM)	ε ($M^{-1}cm^{-1}$)	K (M^{-1})
	SDS/CE/W			CTAB/CE/W	
0	5.4	-	0	760.1	-
1	5.2	802.75	1	656.0	618.69
4	5.0	647.44	4	674.2	515.69
6	4.7	431.06	6	683.4	397.20
10	4.3	345.13	10	694.1	196.03

COMPARATIVE ACCOUNT OF BINDING

The purpose of studying the additive effect of CE in surfactant/W mixture was to check the influence of CE on the micellization of both surfactants (SDS and CTAB) in the ternary mixtures. Due to the hydrophobic interactions between the nonpolar tails of the sur-

factant monomers to form the micelle core and the repulsive interactions between the micellar head groups which are pushing each other on the surface of the micelle, micelles are formed at the cmc. The presence of counter-ions on the surface of micelles helps in their simultaneous stabilization. However, presence of an additive like CE greatly affects the stabilization of the systems as CE is distributed between the aqueous and micellar phases.

SDS belongs to a category of anionic surfactants in which Na^+ is the counterion. Whereas, CTAB belongs to a category of cationic surfactants in which Br^- is the counterion and it is known that cations like Na^+ have a significant affinity towards the cavity of crown ether molecules, whereas, anions like Br^- have least affinity towards the cavity of crown ether molecules. Experimental data indicates that in case of SDS, a significant binding is observed over the measured concentration range of the CE. This is because of the fact that in case of SDS, CE cavity undergoes strong electrostatic interactions with Na^+ in order to form the inclusion complex. Thus in order to form complex with the CE cavity Na^+ can easily be dissociated from the monomer leading to the formation of loose aggregates. The complex draws the counterion away from the sulfate head group,

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increasing the repulsion between head groups, thereby inducing a decrease in micellar size and a corresponding greater surface curvature. The presence of the Na^+-CE complex in the palisade layer, of course helps in the stabilization of the micelles but the overall micelle-solution interfacial interactions remains almost the same due to the similar nature of the micelle-solution interface in the absence and presence of CE. Addition of CE may reduce the hydration of micelle surface and increase the repulsive forces between ionic head groups because of the increase of the charge density of micelle surfaces. It can be concluded that the crown ether- sodium complex is partially associated to the micelle.

However, in case of CTAB, Br^- has non-interacting nature for the CE cavity. Thus in order to form micelles in presence of the CE cavity Br^- can not be easily dissociated from the monomer leading to the formation of aggregates with lower binding. These results show that structures and nature of both the surfactant and CE are major factors which govern the binding of the micellar systems. It seems that with increase in concentration of CE in the CTAB/CE/W ternary mixtures, the micelles start denaturating regardless of the nature of the polar head groups and the hydrophilic interactions which are the prime factors responsible for the micellar stability in case of SDS/CE/W ternary mixtures. It can be concluded that the transfer of the surfactant molecules from monolayers to the bulk solvent by the addition of CE seems to affect the degree of Br^- counter- ion binding to the micelles. It can be attributed to the salvation of Br^- ions by the water molecules due to the structure breaking properties of Br^- ions. This again confirms the strong hydrophobic interactions of the CTAB/CE complex. Addition of CE to the aqueous surfactant solutions enhances the repulsive interactions between the polar heads of CTAB at the micellar surfaces and micellization becomes unfavourable. However, increase in concentration of CE causes a decrease in the binding of both surfactants over the measured concentration range of the CE. This may be attributed to the increase of steric interactions.

CONCLUSION

Inclusion complexes of SDS and CTAB in aque-ous media both in absence and presence of 15- crown-5ether has been investigated with the help of UV/visible spectroscopy. Results show the in presence of CE, micellization of SDS is more favorable as compared to CTAB. The molar absorption coefficient 'ε' and the binding constant K value indicates that the association between CE and SDS is more favorable than CE and CTAB. The results also indicate that the association of CE and surfactants decreases with the increase in concentration of CE.

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