



## STUDY AT A MOLECULAR LEVEL OF THE TRANSFER PROCESS OF ANIONIC, CATIONIC AND NON-IONIC SURFACTANTS FROM WATER TO $\beta$ -CYCLODEXTRIN

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### ABSTRACT

Density and sound velocity data for aqueous solutions at 303K containing Sodium dodecyl benzene sulfonate (SDBS), Cetyl trimethyl ammonium bromide (CTAB) and Tween 20 in the absence and presence of  $\beta$ -Cyclodextrin were analyzed to calculate the apparent molar volume and adiabatic compressibilities. For the binary systems  $\Phi_v$  and  $\Phi_k$  values of the pure surfactants in water have been obtained as a function of the concentration. For the ternary systems, remarkable increases of both the molar volume and compressibility of the surfactant at infinite dilution with respect to the value in water is observed. The positive molar compressibility of the surfactant, when it is forming the complex, compared to the negative value in pure water, proves the hydrophobic components of the interaction. Both molar volumes and compressibility of the surfactants are the same in the absence and in the presence of  $\beta$ -CD at high surfactant concentrations, indicating the non participation of the complex into the micelles and the CMCs are displaced. Using FTIR spectroscopy, the complexation of  $\beta$ -CD at high with anionic, cationic and non-ionic surfactants.

**Keywords:**  $\beta$ -cyclodextrin, sodium dodecyl benzene sulfonate, cetyl trimethyl ammonium bromide, tween 20.

### INTRODUCTION

Cyclodextrins (CD) are a family of macro cyclic oligosaccharides and shaped like truncated cones with relatively hydrophobic hollow cylindrical cavities. The cavity provides an environment favorable for the binding of organic solutes that contain hydrocarbon (or) fluorocarbon moieties. Among the several kinds of driving forces that may be involved, hydrophobic interaction has been implicated as an important factor favoring the formation of the cyclodextrin inclusion compounds [1-3].  $\beta$ -CD is known as one of the most efficient complex agents because of its suitable structure, in which the characteristic hollow truncated cone shape of CDs is combined with a medium size apolar cavity. The hydrophobic-hydrophilic balance that exists between the inner and external surface of the macrocycle is responsible for the formation of complexes through non-covalent interactions with molecules that fit into the cavity [4-5]. The uses of surfactants, as target molecules, offer certain advantages to understand the thermodynamics of complexation. Since it is easy to modulate their properties to study the effect that a determined factor may have in the process (e.g., the polar nature of the head, charge, length of the hydrocarbon tail, etc.) These variables affect the binding constants and the stoichiometry of the complexes and modify the aggregation properties of surfactants in their aggregation properties. For example, surfactants quite different from the structural point of view from critical micelle concentration (cmc) in a certain extension.

Linear surfactants are interesting families of compounds in the attempt to study the role of hydration-water has in the thermodynamics of complexation and the effect that the length of the hydrocarbon-chain has in the inclusion parameters. To our knowledge only a few papers

take up volumetric studies in system  $\beta$ -CD + surfactant + water. Compressibility investigations are even scarcer, being limited to the studies of Gonzalez-Gaintano et al. (1997), with sodium cholate and decyl trimethyl ammonium bromide (DTAB).

In the present work we report volumetric and compressibility studies of Sodium dodecyl benzene sulfonate (SDBS), Cetyl trimethyl ammonium bromide (CTAB) and Tween 20 in aqueous solutions of  $\beta$ -Cyclodextrin ( $\beta$ -CD). This work aims at the qualitative understanding of surfactant binding to  $\beta$ -CD. This has been achieved by examining the behaviors of apparent molar volume ( $\Phi_v$ ), apparent adiabatic compressibility ( $\Phi_k$ ), surface tension ( $\sigma$ ) and sound velocity number (U) of these surfactants in aqueous solutions of  $\beta$ -CD over a wide concentration range (0.0002-0.0020 molar) in view of the fact that these properties have a direct bearing on the structural consequences of hydrophobic hydration/interactions.

### EXPERIMENTAL TECHNIQUES

Sodium dodecyl benzene sulfonate and Tween 20 were obtained from Lobo chemicals; Cetyl trimethyl ammonium bromide and  $\beta$ -cyclodextrin were obtained from SD fine chemicals. Ultrasonic velocities of solutions were measured, using a multi frequency continuous wave ultrasonic interferometer (model F81, Mittal Enterprises, New Delhi), to an accuracy of  $\pm 0.05\%$  at a frequency of 2 MHz at 303K. The density was measured using a precalibrated specific-gravity bottle at 303K temperatures to an accuracy of  $\pm 2$  parts in  $10^4$ . The viscosity was measured in Ostwald's viscometer to an accuracy of  $\pm 0.2\%$ .



## PHYSICAL PARAMETERS

The various physical parameters were calculated from the measured values of density ( $\rho$ ), viscosity ( $\eta$ ) and ultrasonic velocity ( $U$ ) using the standard formula [6]

$$(i) \text{ Adiabatic compressibility } \beta = \frac{1}{U^2 \rho}$$

$$(ii) \text{ Apparent molar volume } \Phi_v = 1000(d_0 - d)m/d_0 + M/d$$

Where  $d_0$  and  $d$  are densities of solvent and solution, respectively,  $m$  is the molality and  $M$  is the molecular weight of the solute.

$$(iii) \text{ Apparent molar adiabatic compressibilities } \Phi_k = 1000(\beta - \beta_0)m/d_0 + \Phi_v \beta$$

Where  $\beta$  and  $\beta_0$  are adiabatic compressibilities of solution and solvent.

## RESULTS AND DISCUSSIONS

### Surfactant + water

The CMC of the surfactant may be calculated through any property which changes around the critical concentration, e.g., from the plots of density or sound velocity versus the surfactant molality (Figure-1). However, considering that the speeds of sound changes are greater than those of the density around the CMC, we have used the property instead. The method consisted of obtaining the derivatives of the plots, with respect to the surfactant molality, provided that many measurements at close constant intervals of concentration are available.

In Figure-2, the apparent molar volume versus the surfactant concentration is plotted for SDBS, CTAB and Tween 20. Below the CMC, the property changes smoothly with the surfactant concentration and the extrapolations at infinite dilution give the volumes and compressibilities of the monomers. At concentration above the CMC the property increases as a result of micelle formation until a constant value is reached [7].

The positive value corresponds to a higher compressibility of the surfactant when it is forming the micelle, suggesting a more hydrophobic environment, with more free accessible volume than in water, and similar to a liquid hydrocarbon [8].

### Surfactant + $\beta$ -CD + water

The apparent molar volumes are plotted in Figure-4. For SDBS, CTAB and Tween 20 the  $\beta$ -CD concentrations were 0.0002 to 0.0020 mol kg<sup>-1</sup> respectively. In all cases the CMC, calculated from  $U$  data, is reached at concentration above and the pure surfactant is illustrated in the Figure-3. For SDBS the CMC, in the ternary system, is practically  $cmc + molar$  concentration, but with the longest homologues it is less than  $cmc + molar$  concentration of the surfactant. This is an evidence that the stoichiometry of the complex is not only 1:1, but there is also a participation of 2:1 (that is to say, two macrocycles per one molecule of surfactant). The shift of the CMC implies that the competitive equilibrium, due to the affinity of the monomer for the micelle or for the  $\beta$ -CD is

resolved in favor of the latter; that is, only when all of the available cavities are occupied, can the monomers aggregate to form the micelles.

Considering the CMCs in the binding constant at  $1.1 \times 10^3$  for CTAB, from the calculated values it can be observed a dramatic changes in the density, which decreases when increasing the amount of surfactant added, up to a concentration slightly higher than concentration of  $\beta$ -CD. This indicates that the solution volume is increasing to the detriment of the overall mass in the solution, as a consequence of the released water from the cavity. Above the CMC, the slopes for the ternary systems are the same, indicating that the complexes have no effect on the aggregates [9].

It is worth mentioning, in the graph for the apparent properties, the curves for the ternary system reach the curve corresponding to the pure surfactant above its CMC, that is; at the point where the micelles have begun to form. When we want to calculate the micellization property of the Tween 20 with the  $\beta$ -CD, as the difference between the values at high concentrations and at the CMC, it is not possible to give a well-defined difference if an apparent property is considered. However, by plotting the molar property there is no problem in obtaining the values, since for all the  $\beta$ -CD concentrations the curves come together in the monomeric region, or at the very beginning of the micelles, giving always the same increments. It's for the same reason a very good precision in the speed of sound and / or densities is required for the study of these systems, precise enough to obtain the properties instead of the apparent ones [10-11].

The apparent molar compressibility (Figure-5) shows a trend similar to the apparent molar volumes. The plots of  $\Phi_k$  versus molar concentration are less noisy than the plots of  $\Phi_v$  since the relative changes in the compressibility are more important compared to the volumes. This is an indication of the strong influence of the solvation effects involved in the inclusion process [12].

The analysis of the compressibility is more difficult, and it can be done by considering the sum of different contributions, which form some of the driving forces in the complex formation with  $\beta$ -CDs. The water molecules, inside the cavity, are highly structured and present a rather low compressibility with respect to the bulk water. In addition to that the surfactant is exposed to a more hydrophobic environment in the complexed form compared to the monomer state. Thus, we cannot assume that the differences of the cavity upon complexation are negligible [13].

A positive value for the compressibility of the cavity should indicate that the cavity of  $\beta$ -CD will be easier to compress when it is filled with the nonionic surfactant instead of water. The negative value could be explained by the high and negative value of the compressibility of surfactant at the monomer state due to a partial folding of the molecular structure and by strong between the interacting surfactant and  $\beta$ -CDs atomic groups in the cavities. Moreover, the existence of intense hydrogen bond interactions between the hydroxyl groups



of the  $\beta$ -CDs that are forming head-to-head dimeric units and a contribution due to interactions between the hydroxyl groups placed at the rims of  $\beta$ -CD and the chain of the surfactant cannot be excluded.

### FTIR analysis

The FTIR spectra of all the samples were collected and the results indicate the typical characteristics of  $\beta$ -cyclodextrin. The comparison of the FTIR spectrum of  $\beta$ -CD with those of  $\beta$ -CD prepared in the presence of anionic, cationic and non-ionic surfactants is presented in the figure 6. The spectra of neat surfactants are not shown in the figure. A strong band at  $2922.65\text{cm}^{-1}$  in the spectrum of  $\beta$ -CD (Figure-6a) is due to the stretching vibration of  $\text{CH}_2$ , and that at  $1645.57\text{cm}^{-1}$  is due to H-O-H bending of physically absorbed water. Bands at  $1156.34$  and  $1029.79\text{cm}^{-1}$  are assigned to the absorption of C-O, C-O-C of glucose units. The relative intensity of the transmittance band at  $941.66\text{cm}^{-1}$  (C-O-C symmetrical stretching bands of five-membered ring) are the characteristic peaks of the rings of  $\beta$ -CD.

Comparing the spectrum of SDBS, CTAB and Tween 20 to the corresponding bands of surfactant can be found in the FTIR spectrum of  $\beta$ -CD. Additional new bands belonging to surfactant appear in the FTIR spectrum of  $\beta$ -CD prepared in the presence of surfactant small peaks ranging from  $2800$  to  $3000\text{cm}^{-1}$ , which are assigned to the aliphatic C-H stretching modes, associated with the long alkyl tail of SDBS and Tween 20 were detected in the presence of  $\beta$ -CD-SDBS and  $\beta$ -CD-Tween 20. The corresponding bands are  $1648.71$ - $1644.33$ ,  $1156.34$ - $1150.68\text{cm}^{-1}$ . It can be seen that the characteristic surfactant peaks were slightly shifted to short wavelengths when modified with  $\beta$ -CD. For example, the peaks at  $1645.57\text{cm}^{-1}$  were shifted to  $1648.71\text{cm}^{-1}$ ,  $1029.79$ - $1156.23\text{cm}^{-1}$ ,  $941.66$ - $943.33\text{cm}^{-1}$ . This discrepancy could be attributed to the interaction of  $\beta$ -CD on the surface of SDBS.

The presence of  $\beta$ -CD, in Figure-6b, can be judged by the characteristic bands of  $2918.76$ ,  $2850.16$ ,  $1736.99$ ,  $1646.21$ ,  $1156.28$ ,  $1030.11$ ,  $962.83$  and  $858.96\text{cm}^{-1}$ . Hence, the modification of CTAB with  $\beta$ -CD may be confirmed. A similar spectral analysis was applied to the tween 20 and  $\beta$ -CD. The characteristic absorption bands of tween 20 are as follows: the aromatic C-H stretching bands at  $2921.69\text{cm}^{-1}$ ; the skeletal vibration bands of the benzene ring at  $1644.33$ ; the peaks of tween 20 can be confirmed by the bands of  $1735.50$ ,  $1644.33$ ,  $1150.68$ ,  $1030.27$ ,  $942.21$  and  $856.32\text{cm}^{-1}$  are due to the presence of  $\beta$ -CD. From the measurements of FTIR the attachment of  $\beta$ -CD upon the surface of surfactant can be confirmed supporting the successful modification of surfactant by the  $\beta$ -CD molecules.

### CONCLUSIONS

The apparent molar volume and adiabatic compressibilities have been obtained from density and sound velocity data for aqueous solution of SDBS, CTAB and Tween 20 in the presence of  $\beta$ -CD at  $303\text{K}$ . For the

binary systems (surfactant + water), the apparent molar volume and compressibilities of the pure surfactants in water as a function of concentration have been obtained.

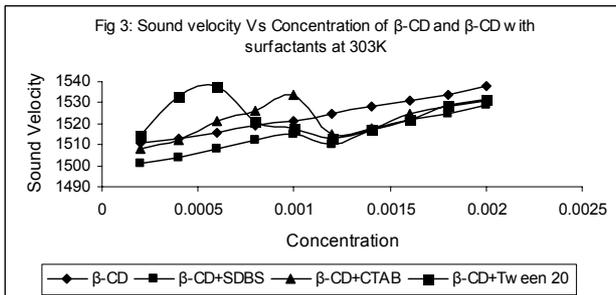
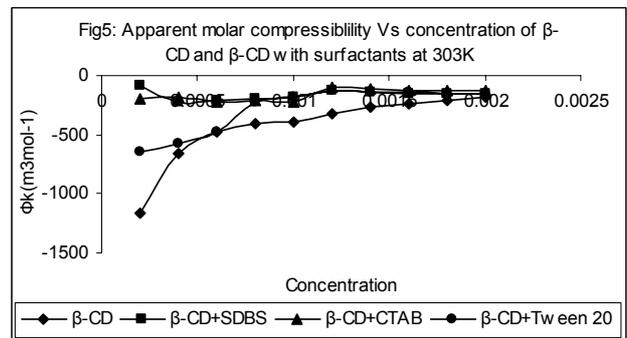
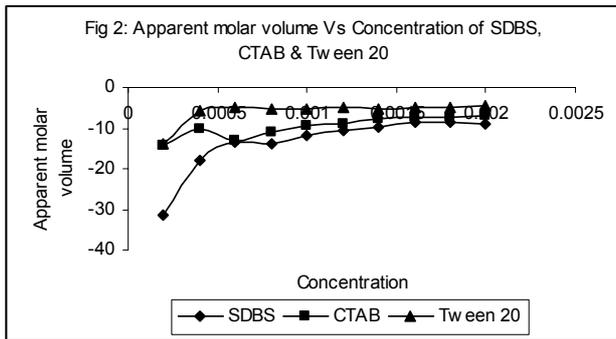
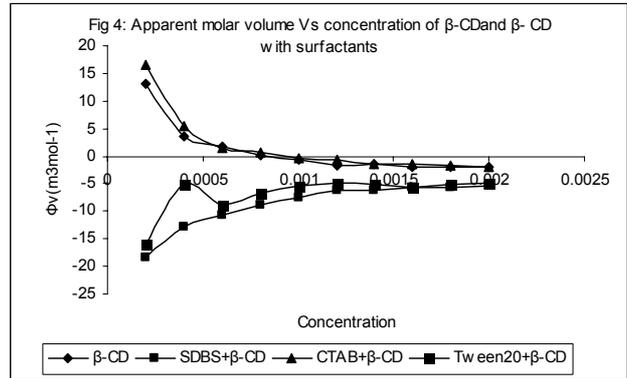
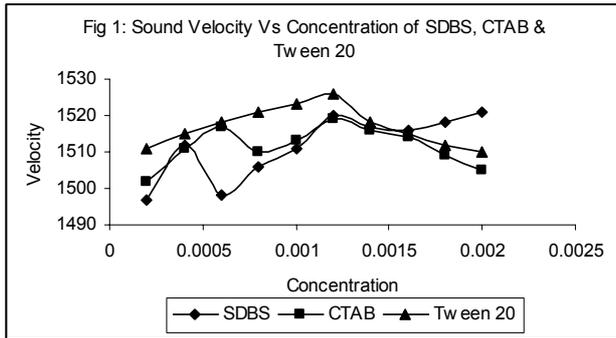
For the surfactants in the presence of  $\beta$ -CD a remarkable increase of the apparent molar volume and compressibility of the monomer at infinite dilution with respect to its value in water is observed. The transfer properties, at infinite dilution, can be discussed in terms of a simple model which considers the balance between the released water from the cavity and the methylene groups of the substrate that enter the macrocycle. Both molar volumes and compressibility are the same, at high surfactant molar concentration, indicating that there is no participation of the complex into the micelles, and the CMCs are shifted in an extension that shows the participation of 2:1 stoichiometry with the longest homologues SDBS, CTAB and tween 20. The analysis of the compressibility with arguments analogous to those of the volume reflects the interactions between the O-H groups of adjacent  $\beta$ -CDs, or suggests the possibility of an inclusion within the cavity of the polar head, as a result of the negative value of the compressibility of the cavity.

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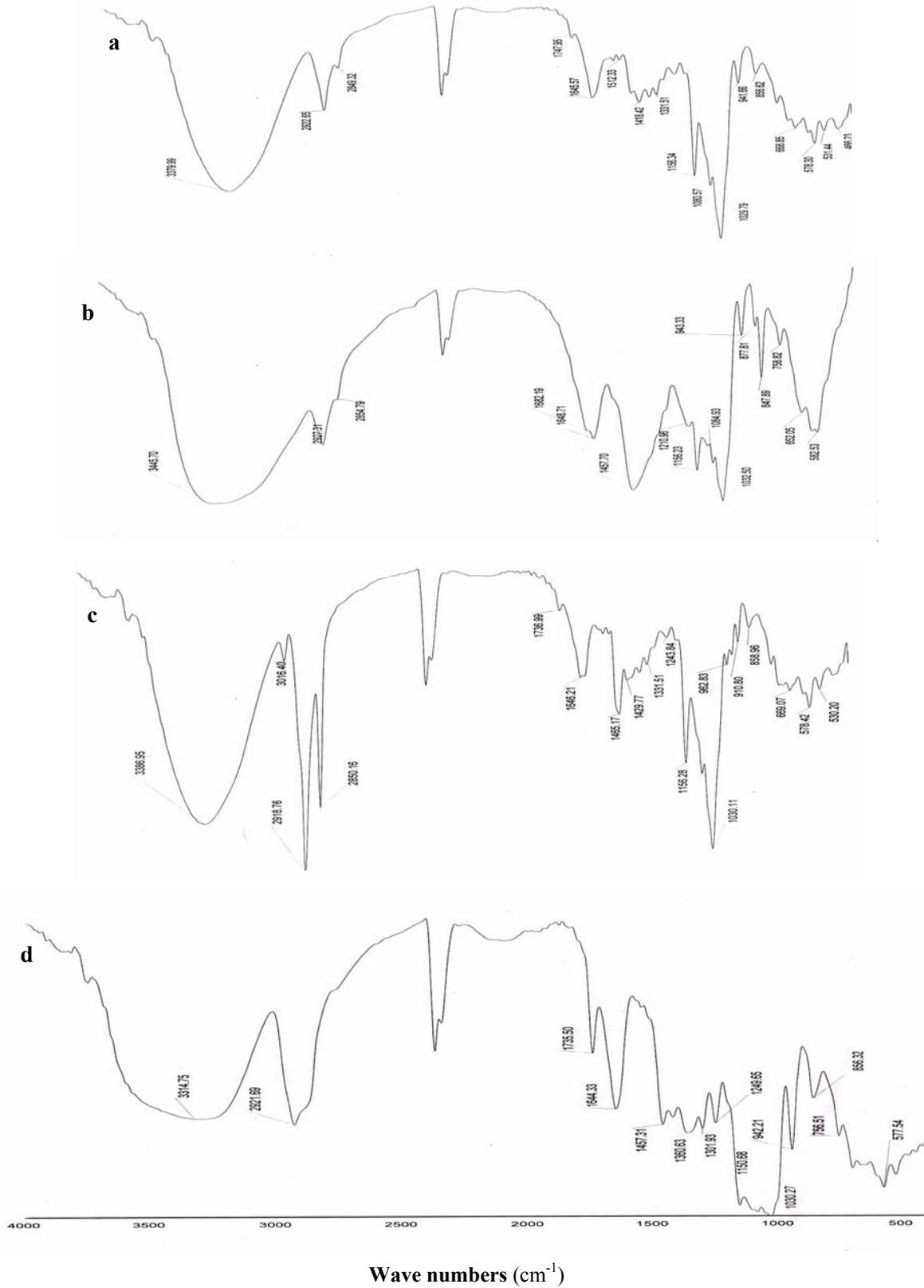


Figure-6. FTIR spectra for (a)  $\beta$ - CD (b)  $\beta$ - CD+SDBS (c)  $\beta$ - CD+CTAB and (d)  $\beta$ - CD + Tween 20.