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Amir Abbas Rafati^a; Fatemeh Safatian^a

^a Faculty of Chemistry, Bu-Ali Sina University, Hamadan, Iran

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Thermodynamic studies of inclusion complex between cetyltrimethylammonium bromide (CTAB) and β -cyclodextrin (β -CD) in water/*n*-butanol mixture, using potentiometric technique

Amir Abbas Rafati* and Fatemeh Safatian

Faculty of Chemistry, Bu-Ali Sina University, Hamadan, Iran

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The behaviour of the inclusion complex consisting of cetyltrimethylammonium bromide (CTAB) and β -cyclodextrin (β -CD) in water/*n*-butanol mixture was studied using ion selective electrodes sensitive to surfactant ions. The experiments were carried out at different temperatures and different composition of water/alcohol. The data obtained indicate that the inclusion complexes S(CD) and S(CD)₂ had formed between CTAB and β -CD in water/alcohol mixture environment. In addition to the 1:1 complex, CTAB formed 1:2 complexes with β -CD. Further investigation showed that K_1 for S(CD) was greater than K_2 for S(CD)₂, and the values of K_i were reduced with increasing butanol concentration. Finally, thermodynamic parameters of the complexation, i.e. ΔH° , ΔG° and ΔS° were also calculated. The obtained thermodynamic data showed that the hydrophobic interaction is the main factor for inclusion complex formation and tendency of complex formation has been reduced with increasing of medium hydrophobicity.

Keywords: inclusion complex; surfactant; cetyltrimethylammonium bromide (CTAB); cyclodextrin; *n*-butanol; ion selective electrode

1. Introduction

Enzymatic hydrolysis of starch usually results in the formation of glucose, maltose, and a long range of linear and branched dextrans. However, a number of different microorganisms and plants produce certain enzymes, called cyclodextrin glucosyltransferases (CGTs), which degrade starch through an intramolecular chain splitting reaction. The cyclic products formed are called cyclodextrins (CDs). Cyclodextrin are cyclic oligosaccharides consisting of (α -1,4)- linked α -D-glucopyranose units, with a somewhat lipophilic central cavity and a hydrophilic outer surface. Due to the chair structure of the glucopyranose units, the CD molecules are shaped like a truncated cone rather than a perfect cylinder. The most abundant natural CDs are α -cyclodextrin (α -CD), β -cyclodextrin (β -CD) and γ -cyclodextrin (γ -CD), containing six, seven, and eight glucopyranose units, respectively. Of these three CDs, β -CD appears to be a most useful pharmaceutical complexing agent because of its complexing abilities, low cost and other properties.

In an aqueous environment, CDs form inclusion complexes with many lipophilic compound molecules through a process in which water molecules located inside the central

*Corresponding author. Email: aa_rafati@basu.ac.ir

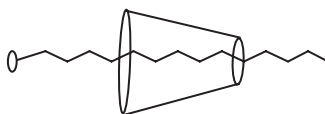


Figure 1. Schematic representation of inclusion complex structure.

cavity are replaced by either the whole guest molecule, or more frequently, by some lipophilic structure of the molecule (Figure 1).

The hydrophobic effect has been implicated as one of the key factors contributing to the relatively strong, noncovalent complexes that are formed between β -CD and apolar guest molecules [1]. β -CD shows amphiphilic character due to an apolar cavity and a hydrophilic annulus consisting of a number of hydroxyl groups. Consequently, unusual solvation effects may occur and, indeed, have been reported in studies of β -CD/guest complexes in mixed (water/organic) solvents [2,3].

Since water molecules located inside the lipophilic CD cavity cannot satisfy their hydrogen-bonding potential, they are of higher enthalpy than bulk water molecules located in the aqueous environment [4].

The main driving force for complex formation at least in the case of β -CD appears to be release of these enthalpy-rich water molecules from the CD cavity which lowers the energy of the system. It is apparent from many reports that host/guest complex formation in aqueous solution should occur with extensive desolvation and resolution of the host, guest, and complex species [5–12].

The natural CDs, in particular β -CD, have limited aqueous solubility, and their complex formation with lipophilic compounds frequently results in precipitation of solid CD complexes. β -CD is more soluble in water in the presence of certain structure-breaking salts such as CaCl_2 or $\text{Ca}(\text{NO}_3)_2$ [13], and in different co-solvent mixtures [14,15], especially in water–alcohol mixtures. This variation in stability of β -CD with the nature of its surroundings involves a modification of its reactivity, particularly towards guest molecules.

In this research, interaction between β -CD and a cationic surfactant, cetyltrimethylammonium bromide (CTAB) is investigated in water/*n*-butanol mixtures. Emf measurements were undertaken to determine the stoichiometry and association constants of CD–surfactant inclusion complexes [16–18]. Our strategy in this study has been to use concentration in the presence and absence of additives to be measured directly. This information can then be used to calculate inclusion complex equilibrium constants under different conditions.

2. Experimental

2.1. Chemicals

A lightly carboxylated PVC available from Aldrich, catalog number 18955-3, labeled to have an average molecular weight of 220,000 and a carboxyl content of 1.8% and used as received. The plastisizer, Elvaloy 742, is a Dupont product. The β -CD used in this work was obtained from Sigma. Thermogravimetric analysis indicated that the β -CD used contained approximately 13.0% water. Cetyltrimethylammonium bromide was obtained from Aldrich and used without further purification. Tetrahydrofuran (THF) and

n-butanol (>99%) were obtained from Merck and used as received. Sodium bromide was a commercial product (Merck), and used as supplied.

2.2. Methods

The membrane ion selective electrode (MISE) selective to CTAB used in the present work was originally constructed to investigate the aqueous mixture solution (water/*n*-butanol) behaviour of the surfactant. The procedures used to construct these MISE are now well documented [19–23].

The ion selective electrode sensitive to surfactant ion was used for the measurement of the free concentration of surfactant ions, $[S]_f$, in equilibrium with CD-surfactant complexes at different conditions. The emf measurements of the surfactant selective electrode were measured relative to a commercial sodium ion electrode (Metrohm 60501–100). In all experiments, the temperature was controlled to within $\pm 0.1^\circ\text{C}$ by circulating thermostatted water (Optima 730) through the jacketed glass cell. The sample solution was continuously stirred using a magnetic stirrer.

3. Results and discussion

The potential of the ion selective electrode was measured relative to the reference electrode. The cell configuration used was:

Surfactant Electrode (MISE) | test solution | reference electrode

At a surfactant concentration below the cmc (critical micelle concentration), the surfactant was completely dissociated. Therefore, the logarithm of surfactant concentration against the emf gives a Nernstian slope. According to the Nernst equation, the following equations can be written for different electrode potentials:

$$E_{\text{sur}^+} = E_{\text{sur}^+}^\circ + \frac{RT}{F} \ln a_{\text{sur}^+} \quad (1)$$

$$E_{\text{Na}^+} = E_{\text{Na}^+}^\circ + \frac{RT}{F} \ln a_{\text{Na}^+} \quad (2)$$

where T is absolute temperature, R is the gas constant, F is Faraday's constant and a_{sur^+} and a_{Na^+} are activities of the surfactant ion and Na^+ , respectively.

The potential of each electrode depends upon the logarithm of the activity of the species. In this way, cells without a liquid junction which can respond to two ionic species concentrations were constructed, namely the surfactant monomer ion, $[S]_f$, and co-ion (where Na^+), $[C]_s$, which comes from the backing electrolyte.

The electrochemical cell can be considered between the surfactant electrode and the sodium electrode (as a reference electrode):

$$E_{\text{cell}} = E_{\text{sur}^+} - E_{\text{Na}^+} \quad (3)$$

$$E_{\text{cell}} = E_{\text{sur}^+/\text{Na}^+}^\circ + 2.303 \frac{RT}{F} \log \left(\frac{[S]_f \gamma_{\text{sur}^+}}{[C]_s \gamma_{\text{Na}^+}} \right) \quad (4)$$

The activity coefficient for an ionic species measures the deviation from ideal behaviour resulting mainly from interionic interactions of an electrostatic nature. At low

ionic strength, the mean activity coefficient of different ions irrespective of charge and shape leads to unity [24]. Based on this, it is reasonable to assume that:

$$\gamma_{\text{Na}^+} \approx \gamma_{\text{sur}^+} \approx 1 \quad (5)$$

and with this assumption the monomer concentration of surfactant ion can be determined below and above the cmc using the equations subsequently. At a constant sodium ion concentration, which applies for this experiment, this assumption leads immediately to:

$$E_{\text{cell}} = E_{\text{sur}^+/\text{Na}^+}^{\circ} + 2.303 \frac{RT}{F} \log[S]_{\text{f}} \quad (6)$$

where

$$E_{\text{sur}^+/\text{Na}^+}^{\circ} = E_{\text{sur}^+/\text{Na}^+}^{\circ} - 2.303 \frac{RT}{F} \log[C]_{\text{s}} \quad (7)$$

A least mean squares method was used for determination of the slope, $2.303 RT/F$, and intercept, $E_{\text{sur}^+/\text{Na}^+}^{\circ}$, for each set of data.

Figures 2–4 show the plot of emf *versus* $\log[S]_{\text{t}}$ in the absence of β -CD and in the presence of β -CD under specified experimental conditions, where $[S]_{\text{t}}$ is the total concentration of surfactant. In the absence of β -CD, it is obvious that at low concentrations of surfactant (below the cmc), the emf is directly proportional to $\log[S]_{\text{t}}$, with the Nernstian slope within an acceptable range (57–60 mV). However, at higher concentrations, the resulting plots show a distinct break at the concentration value characteristic of cmc. In the presence of β -CD, the plot does not obey the Nernstian relationship before the cmc region. The reason is that in the presence of β -CD, an inclusion complex is formed between the surfactant and β -CD. Considering Figures 2–4, the process of complex formation starts at a very low concentration of surfactant and will continue until all β -CD is depleted. Then the CTAB monomer concentration increases and the slope increases drastically, yet the slope is not Nernstian. The present work has studied the interactions of CTAB with β -CD at constant concentration of β -CD ($0.0005 \text{ mol dm}^{-3}$) and NaBr ($10^{-4} \text{ mol dm}^{-3}$) at different temperatures (30, 35 and 40°C). It should be noted that there are no interactions between CD and other ionic species such as Na^+ or Br^- . The potentiometric technique was used in order to obtain $[S]_{\text{f}}$. Here, the curve in the absence of β -CD has been chosen as the standard curve from which E° is obtained. The value of E_{cell} is for the case in which CD is present. In this work, it has been assumed that CDs do not aggregate in water, and are present in monomeric form only.

What is obvious is the formation of an inclusion complex between surfactant (S) and CD. Thus one should be able to define the equilibrium for this reaction:



where $[S]_{\text{f}}$, $[\text{CD}]_{\text{f}}$ and $[\text{S}(\text{CD})]$ are free surfactant monomer concentration, free CD concentration and 1:1 stoichiometric complex concentration, respectively. Although in the beginning the formation of a 1:1 complex seems obvious, there exists the possibility for the formation of a complex with 2:1 stoichiometry or others. The fact that the formation of linking complex results only in 1:1 stoichiometry could be shown with the aid of the Scatchard equation in the form [25,26]:

$$\frac{r}{[S]_{\text{f}}} = K_1 - K_1 r \quad (9)$$

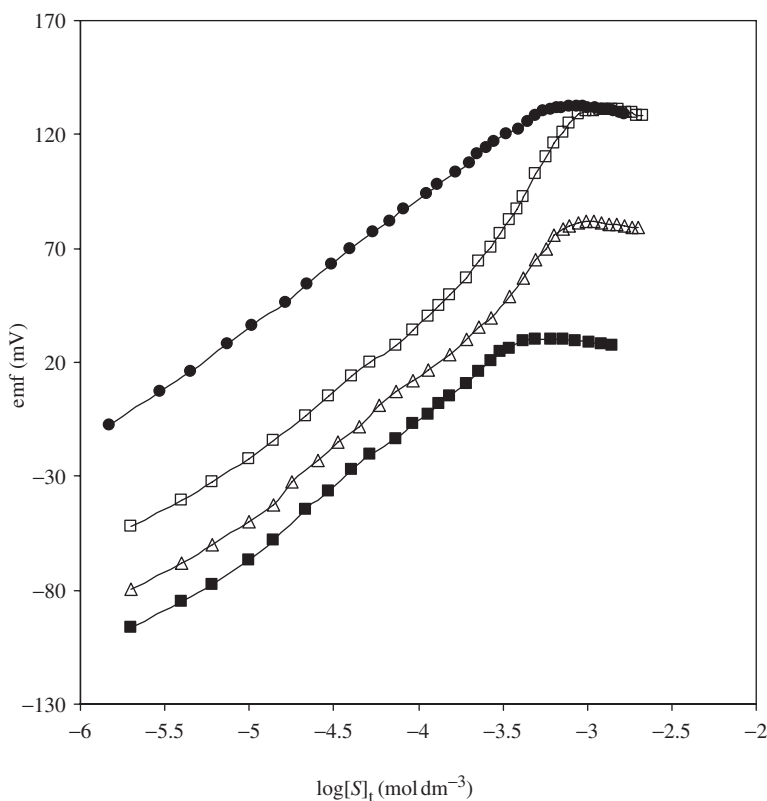


Figure 2. Plot of emf vs. logarithm of total surfactant concentration at 30°C. (●) standard curve in the absence of β -CD; in the presence of β -CD ($5 \times 10^{-4} \text{ mol dm}^{-3}$) and (□) 1%, (Δ) 2% and (■) 4% (v/v) *n*-butanol.

or

$$\frac{1}{r} = \left(\frac{1}{K_1[S]_f} \right) + 1 \quad (10)$$

where

$$r = \frac{\text{Concentration of surfactant complexed with CD}}{\text{Total concentration of CD}} = \frac{[S]_t - [S]_f}{[CD]_t} \quad (11)$$

and $[CD]_t$ is the total concentration of CD.

If $r/[S]_f$ is plotted against r for a 1:1 complex, we expect a straight line with an intercept equal to K_1 and slope equal to $-K_1$. If the plot obtained is not linear (Figure 5), it indicates that we should consider a 2:1 stoichiometry for complex formation (Figure 6).

In this work, the analysis of data under all conditions demonstrates that more than one CD molecule forms a complex with one surfactant ion. Therefore, 2:1 stoichiometry is expected in addition to 1:1 stoichiometry. In this case, some of the complex $S(CD)_2$ is formed according to:



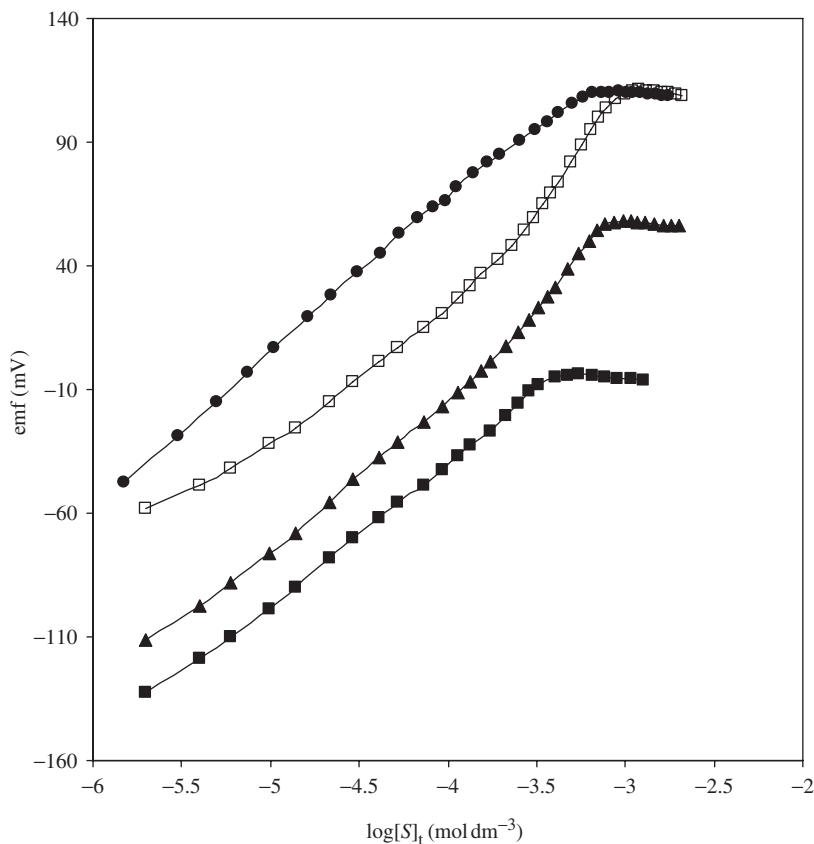


Figure 3. Plot of emf vs. logarithm of total surfactant concentration at 35°C. (●) standard curve in the absence of β -CD; in the presence of β -CD (5×10^{-4} mol dm $^{-3}$) and (□) 1%, (Δ) 2% and (■) 4% (v/v) *n*-butanol.

According to mass balance equations, the following equations have been used:

$$[S]_t = [S]_f + [S(CD)] + [S(CD)_2] \quad (13)$$

$$[CD]_t = [CD]_f + [S(CD)] + 2[S(CD)_2] \quad (14)$$

By using the equations (8), (12), (13), and (14):

$$K_1 K_2 [CD]_f^3 + (K_1 - K_1 K_2 [CD]_t + 2K_1 K_2 [S]_t) [CD]_f^2 + (1 + K_1 [S]_t - K_1 [CD]_t) [CD]_f - [CD]_t = 0 \quad (15)$$

and

$$[S]_f = \frac{[S]_t}{1 + K_1 [CD]_f + K_1 K_2 [CD]_f^2} \quad (16)$$

In the analysis of the data for 2 : 1 complex formation, according to the aforementioned equations, we have used a nonlinear least square fitting program, KINFIT [27]. Using K_1 and K_2 as adjustable parameters, and the criterion that we have used for the “goodness of

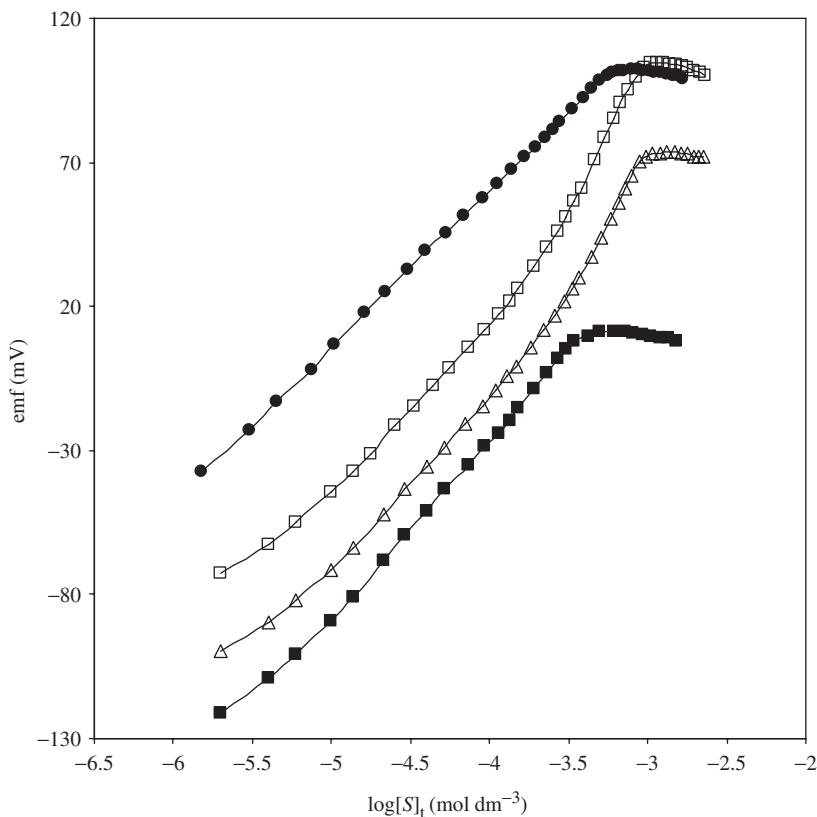


Figure 4. Plot of emf vs. logarithm of total surfactant concentration at 40°C. (●) standard curve in the absence of β -CD; in the presence of β -CD (5×10^{-4} mol dm $^{-3}$) and (□) 1%, (Δ) 2% and (■) 4% (v/v) *n*-butanol.

fit" is the difference between $[S]_f$ calculated *via* equations (15) and (16) and the measured value using the surfactant electrode [equation (6)]. Equation (15) was solved using a Newton method. At first, an approximate K_1 and K_2 are guessed. Then, given each specific experiment, a series of $[CD]_f$ are obtained by solving equation (15) [28]. These $[CD]_f$ values were replacing in +equation (16) and a series of $[S]_f$ are obtained. Now, the obtained free surfactant concentration was compared with experimental $[S]_f$ data from the emf measurements. By this comparison, the new values are obtained for K_1 and K_2 . Then these values would serve as initial values to obtain new K_1 and K_2 . This iteration continued until there was no significant variation in K_1 and K_2 . A typical plot of fitted and experimental emf data is shown in Figure 7. The obtained values for K_1 and K_2 from potentiometric technique are listed in Table 1. The comparison between complexation constant in pure water and water/butanol mixture show that the tendency for inclusion complex formation is decreased with the addition of hydroorganic solvent. Also, the obtained data show that the complexation constants are decreased with increasing amount of butanol, which indicate the role of hydrophobicity on the complexation process. As with adding *n*-butanol in water, the hydrophobicity of media will be decreased. So, this effect caused the lowering of surfactant tendency in order to escape from the media and decrease the complex formation with CD. On the other hand, the solvent molecules

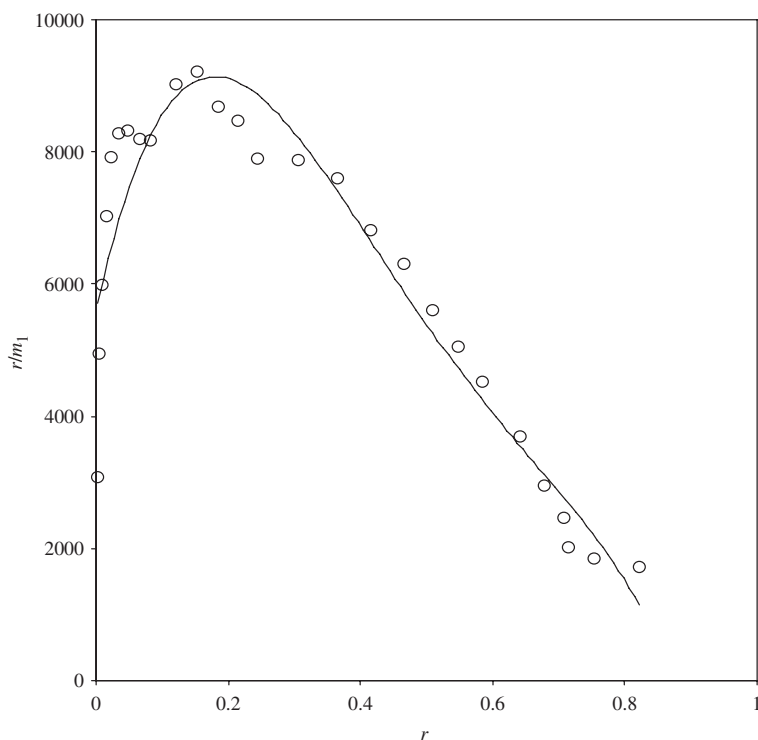


Figure 5. Typical scatchard plot for inclusion complex between CTAB and β -CD ($5 \times 10^{-4} \text{ mol dm}^{-3}$) at 35°C and 1% (v/v) *n*-butanol.

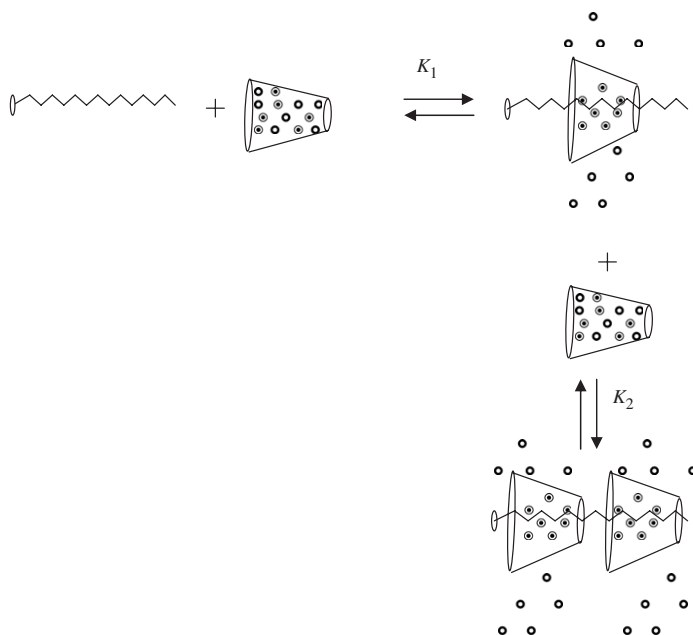


Figure 6. A general representation of the formation of a 2:1 β -CD/CTAB inclusion complex. The (●) symbols denote water molecules and (⊙) symbols denote *n*-butanol molecules.

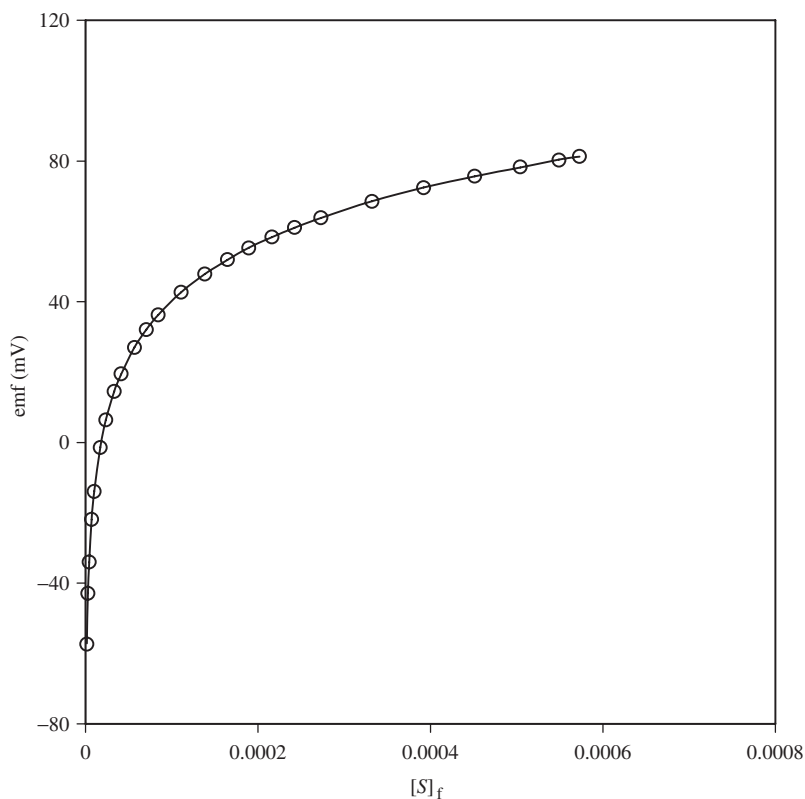


Figure 7. Typical plot of emf data for CTAB vs. surfactant monomer concentration, $[S]_f$, at 35°C and 1% (v/v) *n*-butanol. Continuous curve shows calculated values and open circles refer to experimental values.

Table 1. The calculated values of thermodynamic parameters for complexation of CTAB with β -CD ($5 \times 10^{-4} \text{ mol dm}^{-3}$) at various conditions.

| <i>n</i> -Butanol (%v/v) | <i>T</i> (K) | K_1 ($\text{mol}^{-1} \text{ dm}^3$) | K_2 ($\text{mol}^{-1} \text{ dm}^3$) | ΔG_1 (kJ mol^{-1}) | ΔG_2 (kJ mol^{-1}) | ΔH_1 (kJ mol^{-1}) | ΔS_1 ($\text{J mol}^{-1} \text{ K}^{-1}$) |
|--------------------------|--------------|---|---|--|--|--|--|
| 1% | 303.15 | 25362.15 | 963.54 | -25.56 | -17.32 | | 35.03 |
| | 308.15 | 23330.57 | 1137.39 | -25.77 | -18.03 | -14.94 | 35.14 |
| | 313.15 | 20985.55 | 1066.69 | -25.91 | -18.15 | | 35.03 |
| 2% | 303.15 | 18358.33 | 508.23 | -24.74 | -15.70 | | -89.28 |
| | 308.15 | 12713.03 | 668.06 | -24.21 | -16.66 | -51.81 | -9.57 |
| | 313.15 | 9525.73 | 1477.66 | -23.85 | -19.00 | | -9.28 |
| 4% | 303.15 | 2848.31 | 64.47 | -20.05 | -10.50 | | -287.08 |
| | 308.15 | 1502.65 | 50.07 | -18.74 | -10.03 | -107.08 | -286.66 |
| | 313.15 | 733.06 | 33.15 | -17.18 | -9.12 | | -287.08 |
| 0% (*) | 303.15 | 57962 | 1794 | -27.64 | -18.87 | | 14.10 |
| | 308.15 | 49539 | 1320 | -27.69 | -18.4 | -23.37 | 13.97 |
| | 313.15 | 41112 | 17 | -27.66 | -7.37 | | 13.69 |

*The data were extracted from [12].

involving the cavity of CD do not tend to escape from the CD. This effect along with the previous ones causes the decrease of complexation constants.

The obtained results from this procedure showed that $K_1 > K_2$, which indicates that the formation of a 1 : 1 stoichiometric complex predominates, rather than a 2 : 1 complex. A literature survey showed no data have been reported on inclusion complexes between CTAB and β -CD in water/butanol mixture considering two equilibria, simultaneously. Hence, we could not compare our results with other reported values.

The obtained values of K_1 and K_2 from fitting of the data were used for the calculation of thermodynamic parameters such as ΔH° , ΔG° and ΔS° . The Gibbs free energy of each step in complex formation could be calculated from the following equation:

$$\Delta G^\circ = -RT \ln K_i \quad (17)$$

The enthalpy of complexation was obtained from the temperature dependence of the complexation constant (K_i) using the van't Hoff relation:

$$\frac{d(\ln K_i)}{d(1/T)} = -\frac{\Delta H^\circ}{R} \quad (18)$$

Hence, in this stage plot $\ln K_i$ of against $1/T$ gives a straight line with the slope equal to $-\Delta H^\circ/R$ (Figure 8). The observed thermodynamic calculations showed that K_1 relates in a good manner with temperature as van't Hoff relation. But this behaviour for K_2 is not applicable, so we cannot calculate ΔH° and ΔS° for the second step of complexation.

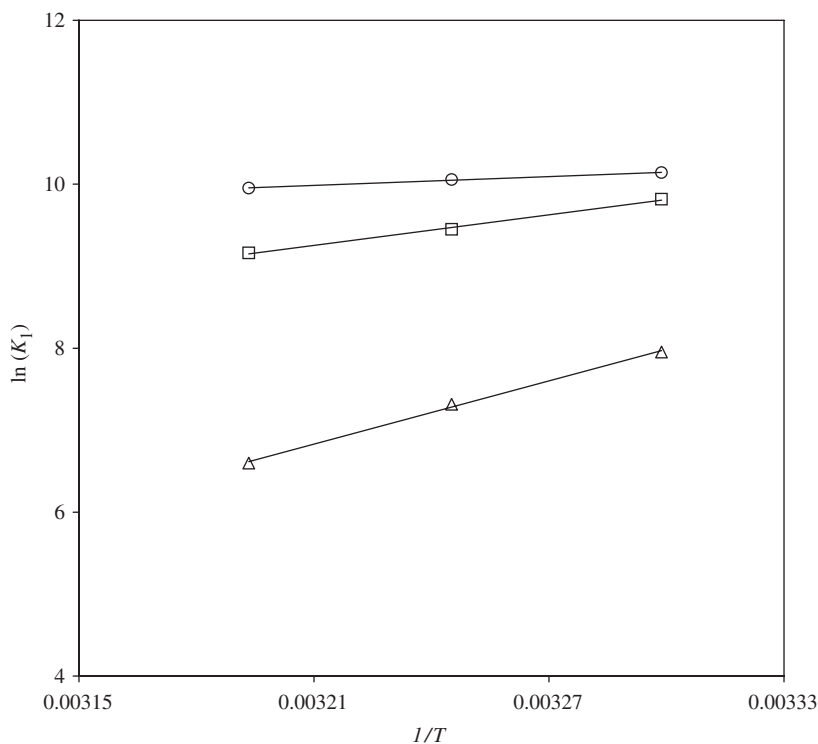


Figure 8. Plot of van't Hoff relation for the first step of inclusion complex formation between CTAB and β -CD ($5 \times 10^{-4} \text{ mol dm}^{-3}$) in (○) 1%; (□) 2% and (Δ) 4% (v/v) *n*-butanol.

Finally, the ΔS° values could be obtained from the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (19)$$

The obtained results are listed in Table 1. The negative values of ΔH° could be attributed to the attraction between the hydrocarbon chain of the surfactant and the hydrophobic interior of CD.

The ΔS° values have decreased with increasing alcohol concentration, for the first step of complexation (1 : 1 stoichiometry). The value of ΔS° is affected by several phenomena. Hydrophobic effects, that can be mainly attributed to the hydrophobic interaction between the alkyl chain and the inner wall of the CD molecule and partly to the release of solvent molecules from the alkyl chain of the surfactant and the cavity of the CD during the penetration process, is one of the most important factors.

The thermodynamic calculations show that the complexation process in the water/butanol mixture is an enthalpy driven process and a negative value for entropy is a prevent parameter to complexation.

In all experiments, the value of K_1 is larger than K_2 , hence the 1 : 1 stoichiometry being preferable to the 2 : 1. The CD structure is such that the inside of the cavity is covered with CH groups thus providing a hydrophobic environment that is favorable to interacting with the hydrocarbon chain of the surfactant. X-ray crystallography shows that the dept and inner diameter of β -CD are 7.8 and 7.8 Å, respectively. The length, l , and diameter, d , of the structural alkyl group with formula C_nH_{2n+1} are calculated from the following equation [28]:

$$l(\text{Å}) \approx 1.5 + 1.265(n - 1) \quad (20)$$

$$d(\text{Å}) \approx \left[\frac{34.89 + 34.25(n - 1)}{1.5 + 1.265(n - 1)} \right]^{1/2} \quad (21)$$

For CTAB surfactant that has 16 carbon atoms in its alkyl chain, using equations (20) and (21) gives the length of the chain as 20.48 Å and the diameter as 5.17 Å. Comparison of these values with the structural characteristics of β -CD shows that there is a good match-fitting between cyclodextrin cavity and surfactant alkyl chain. Of course, in practice the alkyl groups are not always present in structural form, and due to node formation or the existence of trans states, equations (20) and (21) must be corrected.

4. Conclusion

The main conclusion derived from the present study is that the complexation of cationic surfactant ions with CDs and their reactivity towards chelating molecules such as CDs in mixed solvent medium, can be studied by potentiometric technique, using surfactant ion selective electrodes. The electrodes work in a Nernstian response in this medium. This technique allows us to specify solvent effects on the equilibrium between surfactant and β -CD. It has been shown that the increase of complex dissociation with increasing alcohol concentration is mainly due to the strong stabilization of the surfactant ion in solvent by alcohol molecules. Also, we show that the complexation process had formed between CTAB and β -CD in two steps, in mixed water/alcohol medium. Further, investigation showed that K_1 for $S(\text{CD})$ was greater than K_2 for $S(\text{CD})_2$ in water/butanol as well as in pure water. The larger value of K_1 predicts the preferability of the 1 : 1 complex.

The calculated thermodynamic parameters show that the hydrophobic effect has a very important role in the complexation process. The large value of ΔG° indicates that complexation between CTAB and β -CD in mixed solvent (water/butanol) is very favorable.

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