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Electrochemical and Thermodynamic Studies of Inclusion Complex Formation between Tetradecyltrimethylammonium Bromide (TTAB) and β-Cyclodextrin (β-CD)

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The behavior of the inclusion complex consisting of tetradecyltrimethylammonium bromide (TTAB) and β-cyclodextrin (β-CD) was studied using ion selective electrodes sensitive to surfactant ions. Two different methods were used in the construction of the ion selective electrode: (i) Membrane ion selective electrode (MISE) and (ii) Coating wire ion selective electrode (CWISE). The data obtained from two methods showed a consistency between two methods under all conditions. The CWISE method showed a faster response relative to the MISE ones. The experiments were carried out at different temperatures and in different concentrations of cyclodextrin. The data obtained indicate that the inclusion complexes S(CD) and $S(CD)_2$ had formed between TTAB and β-cyclodextrin in an aqueous environment. In addition to the 1:1 complex, TTAB formed 1:2 complexes with β-cyclodextrin. Further investigation showed that K_1 for S(CD) was greater than K_2 for $S(CD)_2$. Finally, thermodynamic parameters of the complexation, i.e., ΔH°, ΔG°, and ΔS° were also calculated.

Cyclodextrins are cyclic oligosaccharides comprised (usually) of six to eight D-glucopyranoside units linked by a 1,4-glycosidic bond. The three most important members of the cyclodextrin family are α-cyclodextrin (α-CD), β-cyclodextrin (β-CD) and γ-cyclodextrin (γ-CD), which possess, respectively, six, seven, and eight glucopyranoside units. β-cyclodextrin shows amphiphilic character due to an apolar cavity and a hydrophilic annulus consisting of a number of hydroxy groups.

Cyclodextrins (CDs) have attracted considerable interest because of their ability to form stable inclusion complexes with a wide variety of inorganic and organic guest molecules in aqueous solution.[1,2] Because of their unusual structure, CDs can form inclusion complexes through noncovalent interactions with molecules that fit into the cavity.[3]

Generally, interaction between a cyclodextrin with an apolar guest molecule in water results in the formation of 1:1 molecular inclusion compounds, in which the guest is included within the cyclodextrin cavity. The inclusion is a thermodynamic equilibrium process with an association constant, K, given by the usual relationship:

$$\mathrm{CD} + \mathrm{S} \rightleftarrows \mathrm{S(CD)} \quad K = \frac{[\mathrm{S(CD)}]}{[\mathrm{S}][\mathrm{CD}]}. \tag{1}$$

Higher equilibria involving the formation of 2:1 complexes or multiple aggregates involving more than one cyclodextrin are common, and often exist simultaneously. The driving force for guest inclusion involves a number of contributions, the importance of which is still a matter of some debate. The main factors of importance are steric fit, release of high-energy water, hydrophobic effects, van der Waals interactions, dispersive forces, dipole–dipole interactions, charge-transfer interactions, electrostatic interactions, and hydrogen bonding.

The hydrophobic effect has been implicated as one of the key factors contributing to the relatively strong, noncovalent complexes that are found between β-cyclodextrin and apolar guest molecules.[4]

It is now generally regarded that both 1:1 and 2:1 cyclodextrin–surfactant complexes can be formed.[5–8] These systems have been the subject of much current interest, with particular emphasis on the determination of complexation constants. Interactions between surfactants and cyclodextrins have been investigated using fluorescence,[9] conductance,[10–15] and surface tension.[16] Emf measurements were undertaken to determine the stoichiometry and association constants of cyclodextrin–surfactant inclusion complexes.[17–19] Our strategy in these studies has been to construct membrane and coated wire electrodes selective to TTAB, allowing the surfactant monomer 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.

Experimental

Chemicals. High-molecular weight poly(vinyl chloride) suitable for ion selective electrodes was obtained from Fluka and used as received. A lightly carboxylated PVC available from Aldrich, catalog number 18955-3, labled to have an average molecular weight of 220000 and a carboxyl content of 1.8% and used as received. The plastisizer, Elvaloy 742, is a Dupont product. The β-cyclodextrin (β-CD) used in this work was obtained from Sigma. Thermogravimetric analysis indicated that the β-CD used contained approximately 13.0% water. Tetradecyltrimethylammonium bromide (TTAB) was obtained from Aldrich and used without further purification. Sodium bromide was a commercial product (Merck), and used as supplied. Tetrahydrofuran (THF) was obtained from Merck and used as received.

Methods. Membrane Ion Selective Electrode (MISE): The membrane ion selective electrode (MISE) selective to TTAB used

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in the present work was originally constructed to investigate the aqueous solution behavior of the surfactant. The procedures used to construct these MISE are now well documented.[20–24]

Coated Wire Ion Selective Electrode (CWISE): The CWISE was constructed as follows: the exposed silver wire, 1–2 mm diameter and 10–20 mm length, was cleaned using 50% nitric acid. The clean wire was then coated with uncharged PVC by repeated dipping in a 7.5% solution of PVC in THF and allowed to dry overnight. The tip of this coating was cut, exposing about 1 mm of bare wire. This was then coated with the PVC conditioned to TTAB to obtain an electroactive coating at the very tip of the wire. For conditioning PVC to the cationic surfactant (TTAB), 200 mg of carboxylated PVC was completely dissolved in 20 mL THF and then added dropwise to a rapidly stirred 500 mL TTAB solution (8×10^{-3} mol dm^{-3}). The precipitated PVC was filtered and washed with distilled water three times and dried in a vacuum oven for 24 h.

The wire was repeatedly dipped in a THF solution containing 0.18 g plastisizer and 0.12 g of conditioned PVC.

Measuring Electrode Response: The ion selective electrode sensitive to surfactant ion was used for the measurement of the free concentration of surfactant ions, $[\mathrm{S}]_\mathrm{f}$, 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 (Methrohm 60501-100). In all experiments, the temperature was controlled to within ±0.1 °C by circulating thermostatted water (Optima 730) through the jacketed glass cell. The sample solution was continuously stirred using a magnetic stirrer.

Results and Discussion

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

Surfactant Electrode (CWISE or 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:

$$E_{\mathrm{sur}^+} = E^{\circ}{}_{\mathrm{sur}^+} + \frac{RT}{F} \ln a_{\mathrm{sur}^+} \tag{2}$$

$$E_{\mathrm{Na}^+} = E^{\circ}{}_{\mathrm{Na}^+} + \frac{RT}{F} \ln a_{\mathrm{Na}^+} \tag{3}$$

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, $[\mathrm{S}]_\mathrm{f}$, and co-ion (where Na^+), $[\mathrm{C}]_\mathrm{s}$, which comes from the backing electrolyte.

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

$$E_{\mathrm{cell}} = E_{\mathrm{sur}^+} - E_{\mathrm{Na}^+} \tag{4}$$

$$E_{\mathrm{cell}} = E^{\circ}{}_{\mathrm{sur}^+/\mathrm{Na}^+} + 2.303\frac{RT}{F}\log\frac{[\mathrm{S}]_\mathrm{f}\gamma_{\mathrm{sur}^+}}{[\mathrm{C}]_\mathrm{s}\gamma_{\mathrm{Na}^+}}. \tag{5}$$

The activity coefficient for an ionic species measures the deviation from ideal behavior 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.[25] Based on this, it is reasonable to assume that:

$$\gamma_{\mathrm{Na}^+} \approx \gamma_{\mathrm{sur}^+} \approx 1 \tag{6}$$

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

$$E_{\mathrm{cell}} = E^{\circ\prime}{}_{\mathrm{sur}^+/\mathrm{Na}^+} + 2.303\frac{RT}{F}\log[\mathrm{S}]_\mathrm{f} \tag{7}$$

where

$$E^{\circ\prime}{}_{\mathrm{sur}^+/\mathrm{Na}^+} = E^{\circ}{}_{\mathrm{sur}^+/\mathrm{Na}^+} - 2.303\frac{RT}{F}\log[\mathrm{C}]_\mathrm{s}. \tag{8}$$

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

Figure 1 shows the plot of emf versus $\log[\mathrm{S}]_\mathrm{t}$ for MISE and CWISE in the absence of β-cyclodextrin under specified experimental conditions, where $[\mathrm{S}]_\mathrm{t}$ is the total concentration of surfactant. It is obvious that at low concentrations of surfactant (below the cmc), the emf is directly proportional to $\log[\mathrm{S}]_\mathrm{t}$, 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.

Figures 2 and 3 show the emf as a function of the $\log[\mathrm{S}]_\mathrm{t}$ in the presence of β-cyclodextrin. This plot does not obey the

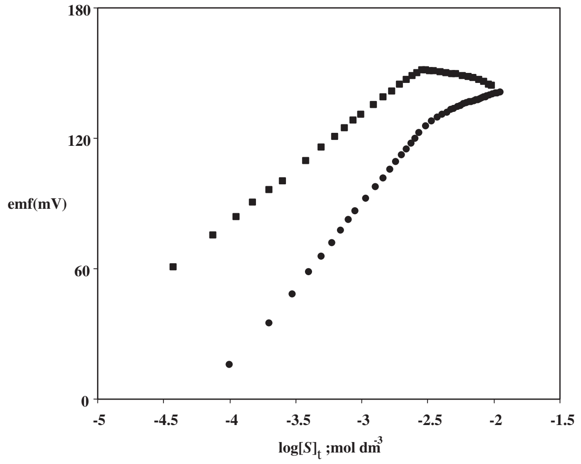


Fig. 1. Plot of emf versus total concentration of TTAB in aqueous solution (10^{-4} mol dm^{-3} of NaBr) at 30 °C by two different ion selective electrode: (■) MISE; (●) CWISE.

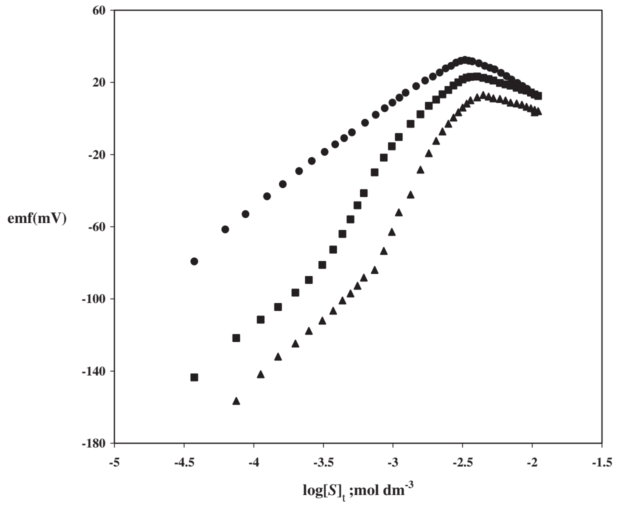


Fig. 2. Plot of emf of MISE versus total concentration of TTAB (●) in aqueous solution; (■) in the presence of 5×10^{-4} mol dm^{-3} of β-CD; (▲) in the presence of 1×10^{-3} mol dm^{-3} of β-CD (at 35 °C and 10^{-4} mol dm^{-3} of NaBr).

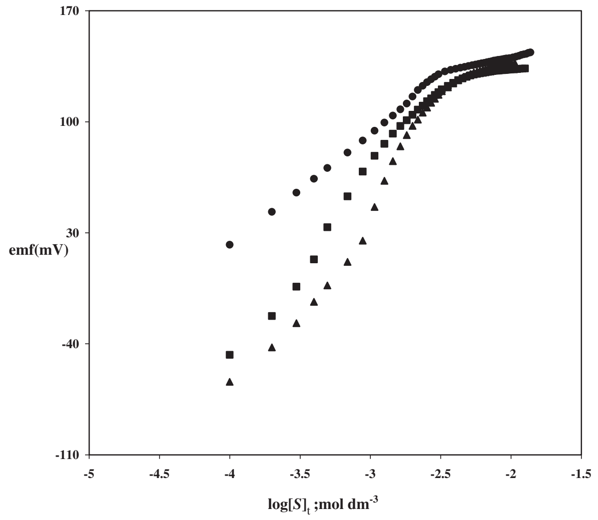


Fig. 3. Plot of emf of CWISE versus total concentration of TTAB (●) in aqueous solution; (■) in the presence of 5×10^{-4} mol dm^{-3} of β-CD; (▲) in the presence of 1×10^{-3} mol dm^{-3} of β-CD (at 35 °C and 10^{-4} mol dm^{-3} of NaBr).

Nernstian relationship before the cmc region. The reason is that in the presence of β-cyclodextrin, an inclusion complex is formed between the surfactant and β-cyclodextrin. Considering Figs. 2 and 3, the process of complex formation starts at a very low concentration of surfactant and would continue until all β-cyclodextrin is depleted. Then the TTAB monomer concentration increases and the slope increase drastically, yet the slope is not Nernstian. The present work has studied the interactions of TTAB with β-cyclodextrin at 10^{-4} mol dm^{-3} NaBr and two different concentrations of β-cyclodextrin (i.e. 10^{-3} and 5×10^{-4} mol dm^{-3}) at 25, 30, 35, and 40 °C. It should be noted that there are no interactions between cyclodextrin and other ionic species such as Na^+ or Br^-. The potentiometric technique was used in order to obtain $[S]_f$. Here, the curve in the absence of β-cyclodextrin has been chosen as the standard curve from which $E^{\circ\prime}$ is obtained. The value of E_{cell} is for the case in which cyclodextrin is present. In this work, it has been assumed that cyclodextrins do not aggregate in water, and are present in monomeric form only.

In the first instance it is necessary to check whether the surfactant (S) and corresponding cyclodextrin (CD) form a 1:1 complex as following:

$$\mathrm{CD} + \mathrm{S} \rightleftarrows \mathrm{S(CD)} \quad K_1 = \frac{[\mathrm{S(CD)}]}{[\mathrm{S}]_f[\mathrm{CD}]_f} \tag{9}$$

where $[S]_f$, $[CD]_f$, and $[S(CD)]$ are free surfactant monomer concentration, free CD concentration, and 1:1 stoichiometric complex concentration, respectively. In this case, we can use the Scatchard equation in the form:[26,27]

$$r/[\mathrm{S}]_f = K_1 - K_1 r \tag{10}$$

where

$$r = \frac{\text{concentration of surfactant complexed with CD}}{\text{total concentration of CD}} = \frac{[\mathrm{S}]_t - [\mathrm{S}]_f}{[\mathrm{CD}]_t} \tag{11}$$

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

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 (Figs. 4 and 5), it indicates that we should consider a 2:1 stoichiometry for complex formation (see Scheme 1). In this scheme, there is no clear evidence in which how CD/TTAB complex perform. It indicates only typically of two-step complex formation, but not as view of structurally. In this work, the analysis of data under all conditions demonstrates that more than one cyclodextrin 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:

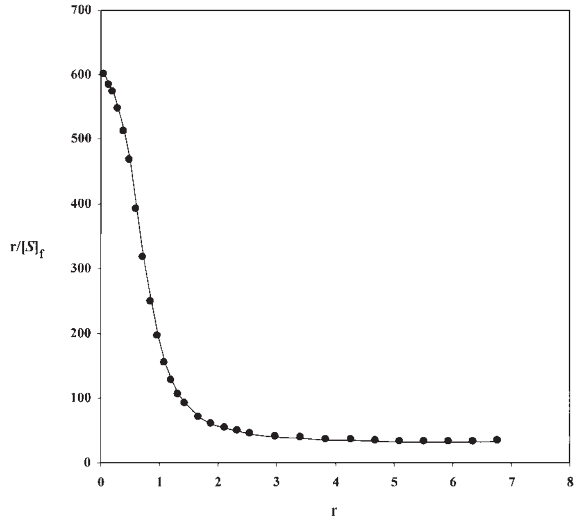


Fig. 4. Scatchard plot for interaction between TTAB and β-CD (0.0005 mol dm^{-3}) at 30 °C, obtained by MISE method.

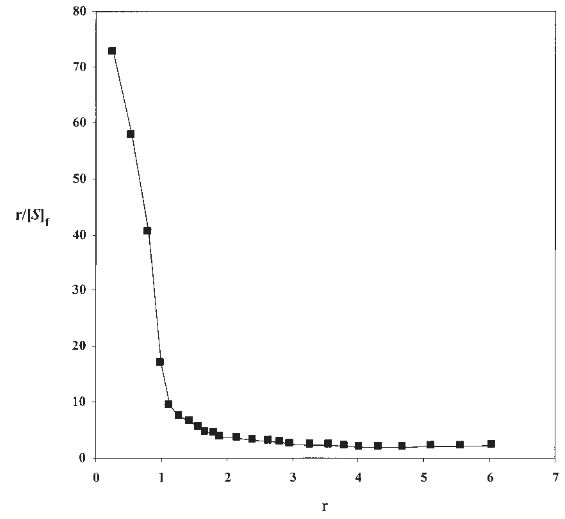
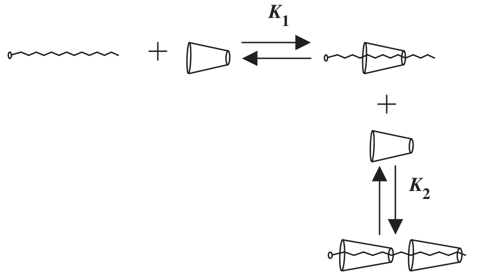


Fig. 5. Scatchard plot for interaction between TTAB and β-CD (0.0005 mol dm^{-3}) at 30 °C, obtained by CWISE method.



Scheme 1. A general representation of the formation of a 2:1 β-CD/TTAB complex.

$$\mathrm{S(CD)} + \mathrm{CD} \rightleftarrows \mathrm{S(CD)_2} \quad K_1 = \frac{[\mathrm{S(CD)_2}]}{[\mathrm{S(CD)}][\mathrm{CD}]_\mathrm{f}}. \tag{12}$$

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

$$[\mathrm{S}]_\mathrm{t} = [\mathrm{S}]_\mathrm{f} + [\mathrm{S(CD)}] + [\mathrm{S(CD)_2}] \tag{13}$$

$$[\mathrm{CD}]_\mathrm{t} = [\mathrm{CD}]_\mathrm{f} + [\mathrm{S(CD)}] + 2[\mathrm{S(CD)_2}]. \tag{14}$$

By using the Eqs. 9 and 12–14:

$$K_1K_2[\mathrm{CD}]_\mathrm{f}{}^3 + (K_1 - K_1K_2[\mathrm{CD}]_\mathrm{t} + 2K_1K_2[\mathrm{S}]_\mathrm{t})[\mathrm{CD}]_\mathrm{f}{}^2$$

$$+ (1 + K_1[\mathrm{S}]_\mathrm{t} - K_1[\mathrm{CD}]_\mathrm{t})[\mathrm{CD}]_\mathrm{f} - [\mathrm{CD}]_\mathrm{t} = 0 \tag{15}$$

and

$$[\mathrm{S}]_\mathrm{f} = \frac{[\mathrm{S}]_\mathrm{t}}{1 + K_1[\mathrm{CD}]_\mathrm{t} + K_1K_2[\mathrm{CD}]_\mathrm{f}^2}. \tag{16}$$

In the analysis of the data for 2:1 complex formation, according to the above equations, we have used a nonlinear least square fitting program, KINFIT.[28] Using K_1 and K_2 as adjustable parameters, and the criterion that we have used for the "goodness of fit" is the difference between $[\mathrm{S}]_\mathrm{f}$ calculated via Eqs. 15 and 16 and the measured value using the surfactant electrode (Eq. 7). Eq. 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 $[\mathrm{CD}]_\mathrm{f}$ are obtained by solving Eq. 15.[6] These $[\mathrm{CD}]_\mathrm{f}$ values were replacing in Eq. 16 and a series of $[\mathrm{S}]_\mathrm{f}$ are obtained. Now, obtained free surfactant concentration was compared with experimental $[\mathrm{S}]_\mathrm{f}$ data from the emf measurements. By this comparison, the new values are obtained for K_1 and K_2. Then these values would served 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 Fig. 6. The obtained values for K_1 and K_2 from MISE and CWISE techniques are listed in Table 1.

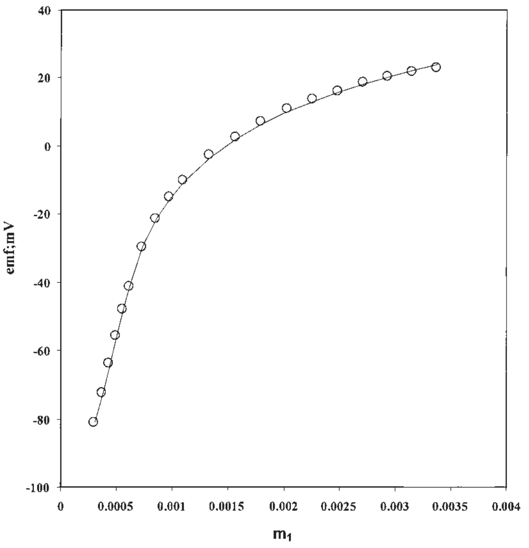


Fig. 6. Typical plot of emf data for CTAB ion selective electrod (MISE) versus surfactant monomer concentration (m_1) at 30 °C and 0.0005 mol dm^{-3} of β-CD. Continuous curve show calculated values and open circle refers to experimental values.

The obtained results from these two procedures showed that $K_1 \gg K_2$, 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 TTAB and β-CD considering two equilibria, simultaneously. Hence, we could not compare our results with other reported values.

Indeed, the variation in the individual K_1 or K_2 for TTAB at different concentrations of β-CD is at worst 10%. In all experiments, we used mean values of K_1 or K_2 for two different concentrations of β-CD to calculate thermodynamic parameters.

The obtained mean 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:

$$\Delta G^\circ = -RT \ln K_i. \tag{17}$$

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

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

and finally the ΔS° values could be obtained from the following equation:

Table 1. The Complexation Constants for the Inclusion Complexes between TTAB and β-CD at Various Concentration of β-CD and Temperatures

		MISE Method				CWISE Method			
$T/°\mathrm{C}$	$[\mathrm{CD}] \times 10^3$ $\mathrm{mol\,dm^{-3}}$	K_1 $\mathrm{mol^{-1}\,dm^3}$	Mean $\mathrm{mol^{-1}\,dm^3}$	K_2 $\mathrm{mol^{-1}\,dm^3}$	Mean $\mathrm{mol^{-1}\,dm^3}$	K_1 $\mathrm{mol^{-1}\,dm^3}$	Mean $\mathrm{mol^{-1}\,dm^3}$	K_2 $\mathrm{mol^{-1}\,dm^3}$	Mean $\mathrm{mol^{-1}\,dm^3}$
25	0.5	65110	64270 ± 1680	288	182 ± 106	60130	62415 ± 4571	200	195 ± 9
	1	63430		76		64701		191	
30	0.5	53891	54747 ± 1713	148	124 ± 24	51233	52979 ± 3492	235	177 ± 57
	1	55604		100		54725		120	
35	0.5	48399	48930 ± 1062	126	107 ± 38	47351	48536 ± 2370	93	88 ± 10
	1	49461		88		49721		83	
40	0.5	43554	50277 ± 963	17	24 ± 4	40867	41291 ± 844	38	33 ± 11
	1	57001		21		41715		27	

Table 2. The Calculated Values of Thermodynamic Parameters for Complexation of TTAB with β-CD Based on Mean Values of Complexation Constants by Two Techniques

Method	$T/°\mathrm{C}$	K_1 $\mathrm{mol^{-1}\,dm^3}$	$\Delta G°_1$ $\mathrm{kJ\,mol^{-1}}$	$\Delta H°_1$ $\mathrm{kJ\,mol^{-1}}$	$\Delta S°_1$ $\mathrm{J\,mol^{-1}\,K^{-1}}$	K_2 $\mathrm{mol^{-1}\,dm^3}$	$\Delta G°_2$ $\mathrm{kJ\,mol^{-1}}$	$\Delta H°_2$ $\mathrm{kJ\,mol^{-1}}$	$\Delta S°_2$ $\mathrm{J\,mol^{-1}\,K^{-1}}$
MISE	25	64270	−27.44	−19.84	25.45	182	−12.89	−96.06	−278.95
	30	54747	−27.49		25.23	124	−12.14		−276.83
	35	48930	−27.66		25.35	107	−11.97		−272.89
	40	43544	−27.81		25.41	24	−8.27		−280.35
CWISE	25	62415	−27.37	−20.60	22.70	195	−13.07	−93.13	−268.51
	30	52979	−27.41		25.48	177	−12.06		−267.41
	35	48530	−27.64		25.85	88	−11.47		−264.99
	40	41291	−27.67		25.58	33	−9.10		−268.32

$$\Delta G° = \Delta H° - T\Delta S°. \tag{19}$$

The obtained results are listed in Table 2. The negative values of $\Delta H°$ could be attributed to the attraction between the hydrocarbon chain of the surfactant and the hydrophobic interior of CD. The $\Delta S°$ values for the first step of complexation (1:1 stoichiometry) are positive, but these values are negative for the second step. The difference in sign of $\Delta S°$ for complexation of β-CD with TTAB (i.e., $\Delta S° > 0$ for K_1 and $\Delta S° < 0$ for K_2) is due to the presence of three $\Delta S°$, in which $\Delta S° = \Delta S°_\mathrm{a} + \Delta S°_\mathrm{b} + \Delta S°_\mathrm{c}$, where:

I) $\Delta S°_\mathrm{a}$: refers to the disordering of the water structure around the hydrocarbon chain of the surfactant, in which $\Delta S°_\mathrm{a} > 0$.

II) $\Delta S°_\mathrm{b}$: according to the structure of CD in aqueous solution, the slightly apolar cyclodextrin cavity is occupied by water molecules, which are energetically unfavored (polar–apolar interaction), and therefore can be readily substituted by appropriate "guest molecules" which are less polar than water (i.e., surfactant hydrocarbon chain). Therefore, the withdrawing of the water molecules from the CD cavity results in $\Delta S°_\mathrm{b} > 0$.

III) $\Delta S°_\mathrm{c}$: refers to association of species, i.e., CDs and surfactant molecules, in which $\Delta S°_\mathrm{c} < 0$.

The resultant sum of these three $\Delta S°$ ($\Delta S°_\mathrm{tot} = \Delta S°_\mathrm{a} + \Delta S°_\mathrm{b} + \Delta S°_\mathrm{c}$) determines the sign of $\Delta S°$.

The value of $\Delta S°$ 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 water 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.

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 cyclodextrin 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 depth 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:[6]

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

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

For TTAB surfactant that has 14 carbon atoms in its alkyl chain, using Eqs. 20 and 21 gives the length of the chain as 17.95 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, Eqs. 20 and 21 must be corrected.

Conclusion

β-Cyclodextrin forms inclusion complexes in 1:1 and 2:1 ratios with TTAB. 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 TTAB and β-CD is very favorable. Also, there is good consistency between obtained data from two techniques, i.e., MISE and CWISE.

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