

A study of the properties of the 1 : 1 inclusion complex of β -cyclodextrin with cetyltrimethylammonium bromide

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Abstract

The properties of the 1 : 1 inclusion complex of β -cyclodextrin (β -CD) with cetyltrimethylammonium bromide (CTAB) were investigated by pyrene and 1-pyrene butyric acid fluorescence. It is shown that in the 1 : 1 CTAB/ β -CD inclusion complex the hydrophobic alkyl chain is included in the β -CD cavity, with the majority of the chain protruding into the bulk phase with the counterion binding to the polar head. In aqueous solution this 1 : 1 CTAB/ β -CD inclusion complex aggregates and micellizes into micelles of which the interior hydrophobic region (the Stern layer and micelle core) is less polar than that of CTAB and its critical micelle concentration is $2.05 \times 10^{-3} \text{ mol l}^{-1}$, which is in agreement with the value determined by surface tension.

1. Introduction

It is well known that cyclodextrins strongly complex with surfactant molecules [1–3], and it is generally believed that the surfactant forms a 1 : 1 complex with β -cyclodextrin (β -CD) [4,5]. Usually, the stoichiometry and association constant of the surfactant/cyclodextrin are determined [1,4]. However, the behavior of the inclusion complex in aqueous solution is still unknown, although it has been reported that in a surfactant- α -CD complex, a 4-carbon containing alkyl chain is included in the α -CD cavity, with the major portion of the alkyl chain protruding into the bulk phase, and the counterion binding to the polar head [7]. Recent reports indicate that the 1 : 1 surfactant/ β -CD inclusion complex is the hydropho-

bic source inducing the aggregation of the micelle [6]. In order to understand how the β -CD affects the aggregation and micellization of the surfactant it is necessary to study the properties of the 1 : 1 surfactant/ β -CD complex itself.

In this Letter, pyrene and 1-pyrenebutyric acid were employed as fluorescence probes to identify the 1 : 1 inclusion complex of β -CD with cetyltrimethylammonium bromide (CTAB). The surface tension was measured by means of the biggest bubble pressure method [8].

2. Experimental

CTAB was a CP reagent from the Shanghai First Chemicals Factory. β -CD (Suzhou Gourment Factory) was recrystallized twice. Pyrene and 1-

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pyrenebutyric acid (PBA) were the products of Aldrich Ltd. The 1 : 1 CTAB/ β -CD was obtained by mixing equal molar amounts of β -CD and CTAB.

Corrected fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. The excitation wavelength of pyrene and PBA was 335 and 340 nm respectively; the slits for the excitation and emission monochromators were both 2.5 nm. The surface tension of the 1 : 1 CTAB/ β -CD solution was measured as in the literature [8]. All experiments were conducted at room temperature.

3. Results and discussion

1-Pyrenebutyric acid (PBA) is an ionic pyrene derivative. Ionic surfactant molecules can induce the formation of excimers of PBA in aqueous solution [9]. CTAB, an ionic surfactant, can induce an excimer of PBA due to the electrostatic interaction between the CTAB cation and anion of PBA to form a neutral association compound which is more hydrophobic than CTAB itself. When CTAB is included in the β -CD cavity, the formation of the excimer may be changed. Fig. 1 shows the fluorescence spectra of PBA in CTAB and the 1 : 1

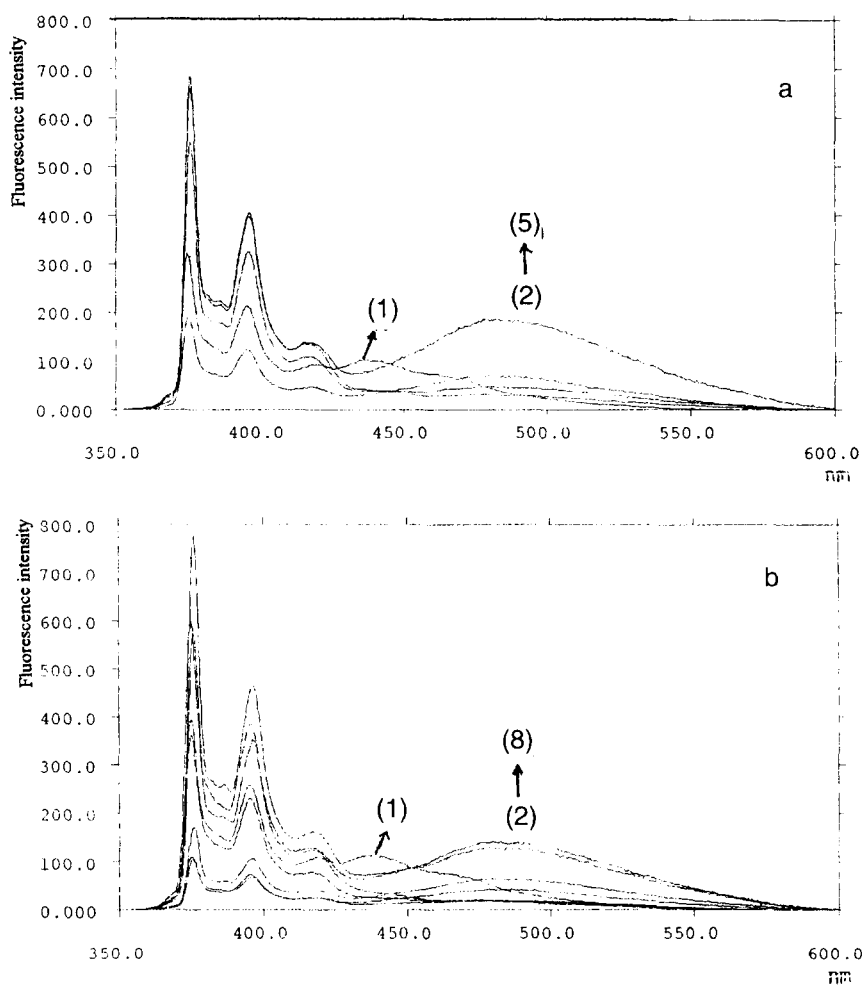


Fig. 1. Fluorescence spectra of PBA in CTAB (a) or 1 : 1 CTAB : β -CD (b) aqueous solutions. [PBA]: $5.0 \times 10^{-5} \text{ mol l}^{-1}$. (a) 10^3 [CTAB] mol l^{-1} : (1) 0, (2) 0.5, (3) 1.0, (4) 1.5, (5) 2.0. (b) 10^3 [1 : 1 CTAB : β -CD] mol l^{-1} : (1) 0, (2) 0.5, (3) 1.0, (4) 1.5, (5) 2.0, (6) 2.5, (7) 3.0, (8) 3.5.

CTAB/ β -CD aqueous solution respectively. It can be noted that the two group spectra are similar. The wavelength values of maximum emission are not changed with the introduction of β -CD in 1:1 CTAB/ β -CD solution compared with CTAB solution; furthermore, the intensity of the excimer increases on increasing the concentration of CTAB or 1:1 CTAB/ β -CD. This indicates that CTAB or 1:1 CTAB/ β -CD solution provides a similar microenvironment for PBA. It has been reported that in the surfactant- α -CD complex, a 4-carbon containing alkyl chain is included in the α -CD cavity, with the major portion of the alkyl chain protruding into the bulk phase, and the counterion binding to the polar head [7]. It can be assumed here that CTAB is the hydrophobic alkyl chain included in the β -CD cavity and the major chain protruding into the bulk phase, with the counterion binding to the polar head. Therefore, it is easy to understand that in 1:1 CTAB/ β -CD solution there still forms an excimer of PBA in spite of the presence of β -CD. However, in 1:1 CTAB/ β -CD, for the CTAB hydrophobic chain tail included in the β -CD cavity, the interaction between CTAB monomer molecules should be changed. We plot the fluorescence intensity ratios of the excimer (485 nm) to the monomer (375 nm) (I_e/I_m) of PBA vs. CTAB concentration and 1:1 CTAB/ β -CD concentration respectively (Fig. 2). From Fig. 2 we can note that the concentration of 1:1 CTAB/ β -CD up to the maximum value of I_e/I_m is higher than that

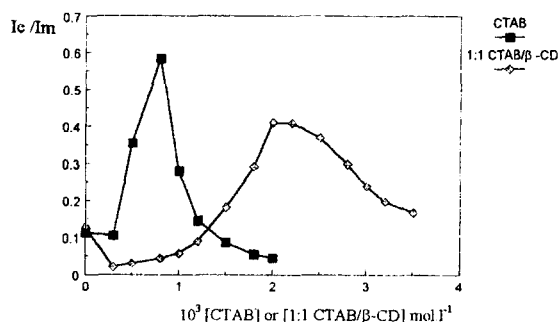


Fig. 2. Excimer (485 nm) to monomer (375 nm) fluorescence intensity ratios vs. CTAB or 1:1 CTAB/ β -CD concentrations. [PBA]: 5.0×10^{-5} mol l^{-1} . 10^3 [CTAB] mol l^{-1} : (1) 0.0, (2) 0.3, (3) 0.5, (4) 0.8, (5) 1.0 (6) 1.2, (7) 1.5, (8) 1.8, (9) 2.0. 10^3 [1:1 CTAB/ β -CD] mol l^{-1} : (1) 0.0, (2) 0.3, (3) 0.5, (4) 0.8, (5) 1.0, (6) 1.2, (7) 1.5, (8) 1.8, (9) 2.0, (10) 2.5, (11) 3.0, (12) 3.2, (13) 3.5.

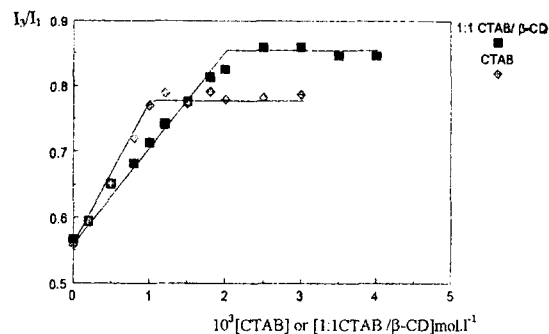


Fig. 3. The ratio of I_3/I_1 of the pyrene fluorescence intensity vs. CTAB or 1:1 CTAB/ β -CD concentrations in aqueous solutions. [pyrene]: 5.0×10^{-6} mol l^{-1} . 10^3 [CTAB] mol l^{-1} : (1) 0.0, (2) 0.2, (3) 0.5, (4) 0.8, (5) 1.0, (6) 1.2, (7) 1.5, (8) 1.8, (9) 2.0, (10) 2.5, (11) 3.0. 10^3 [1:1 CTAB/ β -CD] mol l^{-1} : (1) 0.0, (2) 0.2, (3) 0.5, (4) 0.8, (5) 1.0, (6) 1.2, (7) 1.5, (8) 1.8, (9) 2.0, (10) 2.5, (11) 3.0, (12) 3.5, (13) 4.0.

of CTAB. This shows that due to the CTAB molecule included in the β -CD cavity, the CTAB molecules aggregate in a higher concentration, i.e. the 1:1 CTAB/ β -CD inclusion complex aggregates to form a micelle in aqueous solution.

In order to characterize the micelle properties of the 1:1 CTAB/ β -CD complex, we employ a pyrene probe. As pyrene is an effective fluorescence probe in studies of the characterizations of surfactant molecules [10], the perturbation of the vibronic intensities (especially the variations of I_3 and I_1) has been used as a probe to determine accurately the critical micelle concentration (CMC) of the surfactant and the polarity of the micelle hydrophobic region. Fig. 3 shows the ratios of I_3/I_1 in the presence of CTAB or 1:1 CTAB/ β -CD in aqueous solution. It can be noted that the shapes of the two curves are similar, the only differences being the rate to the maximum value of I_3/I_1 and the maximum value of I_3/I_1 . It also indicates that the pyrene molecule experiences similar changes in the two kinds of solutions. The same experiments in β -CD and 1:1 KBr/ β -CD can further prove that in the 1:1 CTAB/ β -CD inclusion complex the CTAB molecules still have the ability to provide a similar microenvironment for pyrene as free CTAB molecules in spite of the CTAB molecule being included in the β -CD cavity (Fig. 4). The value of the maximum I_3/I_1 of 1:1 CTAB/ β -CD is higher than that of CTAB showing that the polarity of the

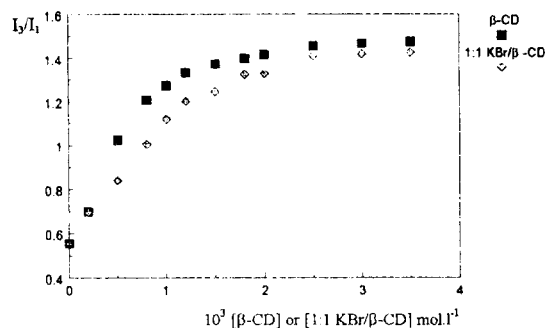


Fig. 4. The ratio of I_3/I_1 of the pyrene fluorescence intensity vs. β -CD or 1:1 KBr: β -CD concentrations in aqueous solutions. [pyrene]: 5.0×10^{-6} mol l^{-1} . 10^3 [β -CD] mol l^{-1} : (1) 0.0, (2) 0.2, (3) 0.5, (4) 0.8, (5) 1.0, (6) 1.2, (7) 1.5, (8) 1.8, (9) 2.0, (10) 2.2, (11) 2.5, (12) 2.8, (13) 3.0, (14) 3.3. 10^3 [1:1 KBr/ β -CD] mol l^{-1} : (1) 0.0, (2) 0.2, (3) 0.5, (4) 0.8, (5) 1.0, (6) 1.2, (7) 1.5, (8) 1.8, (9) 2.0, (10) 2.2, (11) 2.5, (12) 2.8, (13) 3.0, (14) 3.3.

Stern layer and its micelle core is less than that of CTAB, as a leveling of the ratio of I_3/I_1 implies that the pyrene molecules solubilize into the micelle interior hydrophobic region [11] and the maximum value can characterize the polarity of the micelle [12]. Why the micelle hydrophobic region of 1:1 CTAB/ β -CD complex is more hydrophobic than that of CTAB is thought to be the protection by the nonpolar cavity edge of β -CD to the hydrophobic hydrocarbon chain tail. When the ratio of I_3/I_1 is up to the maximum, it indicates the onset of micellization, and the concentration of surfactant at the sharp break equals the CMC [10]. From Fig. 3 we obtain the CMC of CTAB as 1.05×10^{-3} mol l^{-1} , in agreement with the literature value [10], and the CMC of 1:1 CTAB/ β -CD is 2.05×10^{-3} mol l^{-1} . From Fig. 2 we can also obtain the CMC of CTAB and 1:1 CTAB/ β -CD as respectively 0.90×10^{-3} and 2.10×10^{-3} mol l^{-1} . The error in the results originates from the difference between the two probes.

Furthermore, the determination of the surface tension of 1:1 CTAB/ β -CD solutions shows that when the concentration of solution is up to 2.0×10^{-3} mol l^{-1} , the surface tension reaches the minimum value. This can also prove the aggregation and micellization of 1:1 CTAB/ β -CD in aqueous solution.

Due to the CTAB molecule included in the β -CD cavity, the CMC of the 1:1 CTAB/ β -CD inclusion complex is higher than that of CTAB. It is reason-

able that the hydrophobic interaction of the 1:1 CTAB/ β -CD complex is changed with the CTAB hydrophobic chain tail included in the β -CD cavity resulting in the increase of CMC since the increase in volume of the hydrophobic tail in the presence of β -CD and the hydrophilic periphery of β -CD. Whether the CTAB molecule includes from the big edge or the small edge of the β -CD into the cavity is difficult to judge. This is required to be investigated further. Thus the reports [6] that in surfactant solutions β -CD induces the aggregation and micellization of the surfactant can be reasoned by the 1:1 surfactant/ β -CD complex mixing with the surfactant molecule to effect the aggregation and micellization of surfactant molecules.

4. Conclusions

The properties of the 1:1 CTAB/ β -CD inclusion complex were studied. They show that the 1:1 CTAB/ β -CD inclusion complex is the hydrophobic alkyl chain tail included in the β -CD cavity with the major portion of the chain protruding into the bulk phase with the counterion binding to the polar head. In aqueous solution this 1:1 CTAB/ β -CD complex aggregates and micellizes, in which the Stern layer and micelle core is less polar than that of CTAB and its critical micelle concentration is 2.05×10^{-3} mol l^{-1} . Therefore, in surfactant solution, the effect of β -CD on the properties of the surfactant is mainly the result of this 1:1 surfactant/ β -CD inclusion complex.

Acknowledgements

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