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A capillary electrophoresis study on the influence of β-cyclodextrin on the critical micelle concentration of sodium dodecyl sulfate

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Abstract

The influence of β-cyclodextrin (β-CD) on the critical micelle concentration (CMC) of sodium dodecyl sulfate (SDS) was investigated by capillary electrophoresis using anionic chlorophenols as probe molecules at pH 7.0. The variations of the electrophoretic mobility of probe molecules as a function of surfactant concentration in both premicellar and micellar regions in the absence and presence of β-CD was analyzed. The results indicate that, as a consequence of a strong inclusion complexation between β-CD and SDS, the encapsulation of β-CD with probe molecules is greatly diminished, or even vanished, in the presence of SDS. The complexes formed between β-CD and SDS monomers exist predominantly in the form of a 1:1 stoichiometry, while the complexes with a 2:1 stoichiometry reported previously in the literature as a minor component may exist by less than 10%. The elevation of the CMC value of SDS depends not only on the concentration of β-CD in the buffer electrolyte but also on methanol content in the sample solution. The binding constants of probe molecules to β-CD, to surfactant molecules, and to the complexes formed between β-CD and SDS are reported.

Keywords: Critical micellar concentration; Binding constants; Cyclodextrins; Sodium dodecylsulfate; Chlorophenols

1. Introduction

In capillary electrophoresis (CE), surfactants are added either as an electrolyte modifier in the buffer electrolyte in capillary zone electrophoresis (CZE) or used as a pseudo-stationary phase in the separation media in micellar electrokinetic chromatography (MEKC). Thus, a good knowledge of the critical micelle concentration (CMC) of a surfactant is desirable in order to optimize the separation. Various methods, including conductivity [1–4], surface tension [5], light scattering [6,7], spectrophotometry [3,4,8], cyclic voltammetry [9], NMR [10], speed of sound [11], and CE [12–18], were used to determine the CMC values of surfactants. Among them, CE has proven to be a convenient and useful technique for such a measurement. As the CMC value of a surfactant depends on the nature and operating conditions of the buffer electrolyte, e.g. ionic strength, temperature, buffer pH, additive of buffer electrolytes, etc., CE can be conveniently applied to a buffer system containing any electrolyte modifiers.

Three different approaches based on the CE technique have been proposed. The method based on the linear

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relationship of retention factor with micelle concentration was first introduced to yield the CMC value of a surfactant in MEKC [12,13]. However, the CMC values determined by this method were found to be unreliable in some occasions [12,13]. The second approach based on the variation of the effective electrophoretic mobility of a solute as a function of surfactant concentration in the premicellar and micellar regions was proposed [14,15]. Recently, the third method based on the measurements of the electric current of an electrolyte system as a function of surfactant concentration using CE instrumentation at a given voltage was suggested [17]. However, the drawback of this method is that the slopes of the straight lines corresponding to the premicellar and micellar states of surfactant in the concentration range studied need to be different so that the CMC value can be unambiguously determined.

Cyclodextrins (CDs) form inclusion complexes with a variety of hydrophobic and hydrophilic species [19,20], including surfactant molecules. Inclusion complexes with a 1:1 stoichiometry are usually assumed, although inclusion complexes with a 2:1 stoichiometry may occasionally be reported [21].

Cyclodextrins form inclusion complexes with sodium dodecyl sulfate (SDS) [11,22–27]. The addition of β-CD to the premicellar solution system appears to encapsulate surfactant molecules and to shift the equilibrium in favor of the formation of inclusion complexes between surfactant monomers and β-CD, thus, influencing considerably the micellization of surfactant molecules [28]. As a consequence, the CMC value of a surfactant increases with increasing concentration of β-CD [17,22,29–36].

Despite the fact that the CMC value of SDS was determined to be 14.8 m*M* by CE in the presence of 10 m*M* β-CD [17], the interaction of β-CD with SDS and the influence of β-CD on the micellization of SDS is not clearly understood. In this work, pentachlorophenol and 2,3,4,6-tetrachlorophenol are selected as probe molecules. The variations of the effective electrophoretic mobility of these two probe molecules as a function of surfactant concentration in the premicellar and micellar regions in the absence and in the presence of β-CD are analyzed and the binding constants of probe molecules to β-CD and to surfactant molecules are evaluated. The influence of β-CD on the CMC value of SDS and the interaction of β-CD with probe molecules and SDS can thus, be better understood. Moreover, as probe molecules are dissolved in an aqueous solution containing methanol, the influence of methanol content in the sample solution on the CMC value of SDS in the presence of β-CD is also examined.

2. Experimental

2.1. Apparatus

All CE experiments were performed on a Beckman P/ACE System MDQ with a photodiode array detector (Beckman Coulter, Fullerton, CA, USA). Uncoated fused-silica capillaries purchased from Polymicro Technologies (Phoenix, AZ, USA) were used. The dimensions of the capillary are 50.2 cm×50 μm I.D. The effective length of the capillary is 40 cm from the injection end of the capillary. The CE system was interfaced with a microcomputer and a laser printer. System MDQ software (version 1.0.019) of Beckman was used for data acquisition. For pH measurements, a pH meter (Suntex Model SP-701, Taipei, Taiwan) was employed with a precision of ±0.01 pH unit.

2.2. Chemicals and reagents

Pentachlorophenol (PCP) and 2,3,4,6-tetrachlorophenol (TTCP) were purchased from Tokyo Kasei Kogyo (TCI, Tokyo, Japan). β-CD and SDS were obtained from Merck (Germany). Sudam III, used as a micelle marker, was supplied by Janssen (Belgium). Methanol, used as a neutral marker, is of HPLC grade purchased from Mallinckrodt (USA). All other chemicals were of analytical grade. Deionized water was prepared with a Milli-Q system (Millipore, Bedford, MA, USA).

Sample solutions were prepared by dissolving chlorophenols at a concentration of 10 μg/ml in an aqueous solution containing 5–30% methanol. The pH of a phosphate buffer was adjusted to the desired pH value (pH 7.0) by mixing various proportions of a certain concentration of sodium dihydrogenphosphate solution with the same concentration of disodium hydrogenphosphate solution. All buffer solutions, which contained various concentrations of SDS and β-CD and were freshly prepared weekly and stored in a refrigerator before use, were filtered through a membrane filter (0.22 μm).

2.3. Electrophoretic procedure

When a new capillary was used, the capillary was washed 30 min with 1.0 *M* NaOH solution, followed by 30 min with deionized water at 25. Before each injection, the capillary was prewashed for 8 min with running buffer and postwashed for 5 min with deionized water, 5 min with 1.0 *M* NaOH, 5 min with 0.1 *M* NaOH, and 5 min with deionized water to maintain proper reproducibility of run-to-run injections. Sample injections were done in a hydrodynamic mode over 3.5 s under a pressure of 1.0 p.s.i. (1 p.s.i.=6894.76 Pa). The measurements were run at least in triplicate to ensure reproducibility. An applied voltage of 20 kV was selected to keep the total current less than 100 μA in order to avoid experimental complications resulting from Joule heating. The detection wavelength was set at 215 nm. The relative standard deviation of migration time is less than 0.6% (n=5).

2.4. Mobility calculations

The electrophoretic mobility of analytes was calculated from the observed migration times with the equation:

$$\mu_{ep} = \mu - \mu_{eo} = \frac{L_d L_t}{V} \cdot \left(\frac{1}{t_m} - \frac{1}{t_{eo}} \right)$$

where μ_{ep} is the electrophoretic mobility of the analyte tested, μ is the apparent mobility, μ_{eo} is the electroosmotic mobility, t_m is the migration time measured directly from the electropherogram, t_{eo} is the migration time for an unchanged solute, L_t is the total length of capillary, L_d is the length of capillary between injection and detection, and V is the applied voltage.

2.5. Evaluation of binding constants

Theoretical equations for expressing the effective electrophoretic mobility of probe molecules as a function of either β-CD concentration and/or SDS concentration are derived and described in Section 3. The binding constants of probe molecules to β-CD, to SDS monomers, to SDS micelles and to the complexes formed between β-CD and SDS monomers were then evaluated by curve-fitting the predicted mobility data with the experimental mobility data through the utilization of Excel software.

3. Theoretical considerations on electrophoretic mobility

3.1. Influence of cyclodextrins

In an electrophoretic buffer system containing β-CD, the effective electrophoretic mobility of a fully dissociated species of a probe molecule can be phenomenologically expressed as:

$$\mu_{eff} = \alpha_{A^-} \mu_{A^-} + \alpha_{A^- \cdot CD} \mu_{A^- \cdot CD} \quad (1)$$

where α and μ denote the mole fraction and electrophoretic mobility of the ionic species involved. Thus, μ_{A^-} and $\mu_{A^-\cdot CD}$ represent the limiting electrophoretic mobility of the anionic species of a probe molecule (A^-) and the inclusion complex ($A^-\cdot CD$) formed between A^- and CD, respectively. The mole fractions α_{A^-} and $\alpha_{A^-\cdot CD}$, respectively, can be more specifically expressed in terms of the concentration of free CD molecules ([CD]), or the total concentration of CD molecules ($[CD]_t$), and the binding constants of A^- to CD ($K_{A^-\cdot CD}$) as [37,38]

$$\alpha_{A^-} = \frac{1}{1 + K_{A^-\cdot CD}[CD]}$$

and

$$\alpha_{A^-\cdot CD} = \frac{K_{A^-\cdot CD}[CD]}{1 + K_{A^-\cdot CD}[CD]}$$

where $[CD] = [CD]_t/(1 + K_{A^-\cdot CD}[A^-])$. Hence, Eq. (1) can be expressed as: [37,38]

$$\mu_{eff} = \frac{\mu_{A^-} + K_{A^-\cdot CD}[CD]\mu_{A-\cdot CD}}{1 + K_{A^-\cdot CD}[CD]} \quad (2)$$

3.2. Influence of surfactant molecules

In a similar fashion, in the presence of anionic surfactant monomers (S^-) without the addition of cyclodextrins, the effective electrophoretic mobility of an anionic probe molecule can be expressed as:

$$\mu_{eff} = \alpha_{A^-}\mu_{A^-} + \alpha_{A^-\cdot S^-}\mu_{A^-\cdot S^-} \quad (3)$$

where $A^-\cdot S^-$ represents the complex formed between A^- and surfactant monomers (S^-). Likewise, Eq. (3) can be specifically given by the following equation

$$\mu_{eff} = \frac{\mu_{A^-} + K_{A^-\cdot S^-}[S^-]\mu_{A^-\cdot S^-}}{1 + K_{A^-\cdot S^-}[S^-]} \quad (4)$$

where $[S^-]$ and $K_{A^-\cdot S^-}$ represent the concentration of surfactant monomers and the binding constant of the complex formed between A^- and S^-, respectively. For anionic surfactant monomers, the magnitude of $K_{A^-\cdot S^-}$ is expected to be small because of the repulsive interactions between the anionic probe molecule and anionic surfactant monomers.

With surfactant molecules at concentrations greater than the CMC, the effective electrophoretic mobility of an anionic probe molecule is expressed as:

$$\mu_{eff} = \alpha_{A^-}\mu_{A^-} + \alpha_{A^-\cdot S^-}\mu_{A^-\cdot S^-} + \alpha_{A^-\cdot M}\mu_{A^-\cdot M} \quad (5)$$

where $A^-\cdot M$ represents the complex formed between A^- and the anionic micelles. Likewise, Eq. (5) can be expressed as [16]:

$$\mu_{eff} = \frac{\mu_{A^-} + K_{A^-\cdot S^-}[CMC]\mu_{A^-\cdot S^-} + K_{A^-\cdot M}[M]\mu_M}{1 + K_{A^-\cdot S^-}[CMC] + K_{A^-\cdot M}[M]} \quad (6)$$

where $[S^-]$ is equal to the CMC of a surfactant, [M] is the concentration of surfactant micelles, $K_{A^-\cdot M}$ is the binding constant of A^- to the micelles and μ_M is the electrophoretic mobility of anionic micelles.

3.3. Influence of both cyclodextrins and surfactant molecules

In an electrophoretic buffer system containing both cyclodextrins and anionic surfactant monomers,

depending on their concentrations, the interactions of probe molecules with electrolyte modifiers become quite complicated because the following equilibria may be involved:

$$A^- + CD \overset{K_{A^-\cdot CD}}{\rightleftharpoons} A^- \cdot CD$$

$$A^- + S^- \overset{K_{A^-\cdot S^-}}{\rightleftharpoons} A^- \cdot S^-$$

$$S^- + CD \overset{K_1}{\rightleftharpoons} S^- \cdot CD$$

$$S^- \cdot CD + CD \overset{K_2}{\rightleftharpoons} S^- \cdot (CD)_2$$

$$S^- \cdot CD + A^- \overset{K_{S^-\cdot CD\cdot A^-}}{\rightleftharpoons} S^- \cdot CD \cdot A^-$$

$$S^- \cdot (CD)_2 + A^- \overset{K_{S^-\cdot (CD)_2\cdot A^-}}{\rightleftharpoons} S^- \cdot (CD)_2 \cdot A$$

where $K_{S^-\cdot CD\cdot A^-}$ and $K_{S^-\cdot (CD)2\cdot A^-}$ are the binding constant of the complexes formed between A^- and $S^-\cdot CD$ and that of the complexes formed between A^- and $S^-\cdot (CD)_2$, respectively; K_1 and K_2 are the binding constants of the complexes formed between SDS and β-CD and that of the complexes formed between $S^-\cdot CD$ and CD, respectively.

In the absence of surfactant micelles, the effective electrophoretic mobility of an anionic probe molecule may be composed of the following terms:

$$\mu_{eff} = \alpha_{A^-}\mu_{A^-} + \alpha_{A^-\cdot S^-}\mu_{A^-\cdot S^-} + \alpha_{A^-\cdot CD}\mu_{A^-\cdot CD} + \alpha_{S^-\cdot CD\cdot A^-}\mu_{S^-\cdot CD\cdot A^-} + \alpha_{S^-\cdot (CD)_2A^-}\mu_{S^-\cdot (CD)_2A^-} \quad (7)$$

It is noted that the analytical concentration of an anionic probe molecule ($[A^-]_T$), which is equal to $[A^-]+[A^-\cdot S^-]+[A^-\cdot CD]+[S^-\cdot CD\cdot A^-]+[S^-\cdot (CD)_2\cdot A^-]$, can be expressed in terms of $[S^-]$, [CD], and various binding constants as:

$$[A^-]_T = [A^-](1 + K_{A^-\cdot S^-}[S^-] + K_{A^-\cdot CD}[CD] + K_{S^-\cdot CD\cdot A^-}K_1[S^-][CD] + K_{S^-\cdot (CD)_2\cdot A^-}K_1K_2[S^-][CD]^2)$$

Similarly, the total concentration of β-CD ($[CD]_T$), which is equal to $[CD]+[S^-\cdot CD]+[A^-\cdot CD]+[S^-\cdot CD\cdot A^-]+2[S^-\cdot (CD)_2]+2[S^-\cdot (CD)_2\cdot A^-]$, can be expressed in terms of $[S^-]$, [CD], and various binding constants as:

$$\begin{aligned}[CD]_T &= [CD] + K_1[S^-][CD] + K_{A^-\cdot CD}[A^-][CD] \\ &\quad + K_1K_{S\cdot CD\cdot A^-}[A^-][S^-][CD] + 2K_1K_2[S^-][CD]^2 \\ &\quad + 2K_1K_2K_{S\cdot (CD)_2\cdot A^-}[A^-][S^-][CD]^2 \\ &= [CD](1 + K_1[S^-] + K_{A^-\cdot CD}[A^-] + K_1K_{S\cdot CD\cdot A^-}[A^-][S^-] \\ &\quad + 2K_1K_2[S^-][CD] \\ &\quad + 2K_1K_2K_{S\cdot CD_2\cdot A^-}[A^-][S^-][CD])\end{aligned}$$

Likewise, the total concentration of surfactant monomers ($[S^-]_T$), which is equal to $[S^-]+[A^-\cdot S^-]+[S^-\cdot CD]+[S^-\cdot (CD)_2]+[S^-\cdot CD\cdot A^-]+[S^-\cdot (CD)_2\cdot A^-]$, can be expressed as:

$$\begin{aligned}[S^-]_T &= [S^-](1 + K_{A^-\cdot S^-}[A^-] \\ &\quad + K_1[CD] + K_1K_2[CD]^2 + K_1K_{S^-\cdot CD\cdot A^-}[A^-][CD] \\ &\quad + K_1K_2K_{S^-\cdot (CD)_2\cdot A^-}[A^-][CD]^2)\end{aligned}$$

When the existence of the complexes with a 2:1 stoichiometry formed between CD and surfactant monomers is indicative and significant, the last term may not be eliminated. If this is the case, then the effective electrophoretic mobility of an anionic probe molecule in the premicellar concentration region can be specifically expressed as:

$$\mu_{\text{eff}} = \frac{\mu_{A^-} + K_{A^-\cdot S^-}[S^-]\mu_{A^-\cdot S^-} + K_{A^-\cdot CD}[CD]\mu_{A^-\cdot CD} + K_1K_{S^-\cdot CD\cdot A^-}[S^-][CD]\mu_{S^-\cdot CD\cdot A^-} + K_1K_2K_{S^-\cdot (CD)_2\cdot A^-}[S^-][CD]^2\mu_{S^-\cdot (CD)_2\cdot A^-}}{1 + K_{A^-\cdot S^-}[S^-] + K_{A^-\cdot CD}[CD] + K_1K_{S^-\cdot CD\cdot A^-}[S^-][CD] + K_1K_2K_{S^-\cdot (CD)_2\cdot A^-}[S^-][CD]^2} \quad (8)$$

where

$$[CD] = \frac{[CD]_T}{1 + K_1[S^-] + K_{A^-\cdot CD}[A^-] + K_1K_{S^-\cdot CD\cdot A^-}[A^-][S^-] + 2K_1K_2[S^-][CD] + 2K_1K_2K_{S^-\cdot (CD)_2\cdot A^-}[A^-][S^-][CD]}$$

$$[S^-] = \frac{[S^-]_T}{1 + K_{A^-\cdot S^-}[A^-] + K_1[CD] + K_1K_2[CD]^2 + K_1K_{S^-\cdot CD\cdot A^-}[A^-][CD] + K_1K_2K_{S^-\cdot (CD)_2\cdot A^-}[A^-][CD]^2}$$

and

$$[A^-] = \frac{[A^-]_T}{1 + K_{A^-\cdot S^-}[S^-] + K_{A^-\cdot CD}[CD] + K_1K_{S^-\cdot CD\cdot A^-}[S^-][CD] + K_1K_2K_{S^-\cdot (CD)_2\cdot A^-}[S^-][CD]^2}$$

Likewise, based on a similar consideration as described in Section 3.2 and the aforementioned paragraphs of this section, the effective electrophoretic mobility of an anionic probe molecule with surfactants in the micellar concentration region can be specifically expressed as:

$$\mu_{\text{eff}} = \frac{\mu_{A^-} + K_{A^-\cdot S^-}[CMC]\mu_{A^-\cdot S^-} + K_{A^-\cdot CD}[CD]\mu_{A^-\cdot CD} + K_1K_{S^-\cdot CD\cdot A^-}[CMC][CD]\mu_{S^-\cdot CD\cdot A^-}}{1 + K_{A^-\cdot S^-}[CMC] + K_{A^-\cdot CD}[CD] + K_1K_{S^-\cdot CD\cdot A^-}[CMC][CD] + K_1K_2K_{S^-\cdot (CD)_2\cdot A^-}[CMC][CD]^2 + K_{A^-\cdot M}[M]} + \frac{K_1K_2K_{S^-\cdot (CD)_2\cdot A^-}[CMC][CD]^2_{S\cdot CD_2\cdot A^-} + K_{A^-M}[M]_M}{1 + K_{A^-\cdot S^-}[CMC] + K_{A^-\cdot CD}[CD] + K_1K_{S^-\cdot CD\cdot A^-}[CMC][CD] + K_1K_2K_{S^-\cdot (CD)_2\cdot A^-}[CMC][CD]^2 + K_{A^-\cdot M}[M]} \quad (9)$$

Consequently, according to Eqs. (2), (4), (6), (8) and (9), the migration behavior of a probe molecule under various electrophoretic conditions can be predicted, provided that the binding constants and the necessary mobility data are available.

4. Result and discussion

4.1. Electrophoretic mobility as a function of β-CD concentration

Fig. 1 shows the variation of the electrophoretic mobility of the two chlorophenols studied as a function of β-CD concentration in the range 0–9.0 m*M* with chlorophenols dissolved in a 20% (v/v) methanolic solution. The experimental data are shown by the data points, while the predicted curves are represented by the solid lines. As can be seen, the electrophoretic mobility of TTCP decreases more rapidly than that of PCP with increasing β-CD concentration, because the binding constant of TTCP with β-CD is greater than that of PCP with β-CD. According to Eq. (2), the fitting of the predicted mobility curve to the experimental data of these two chlorophenols allows us to evaluate the binding constants of inclusion complexes formed between chlorophenols and β-CD. The binding constants of PCP- and TTCP- complexes evaluated are 280 and 2900

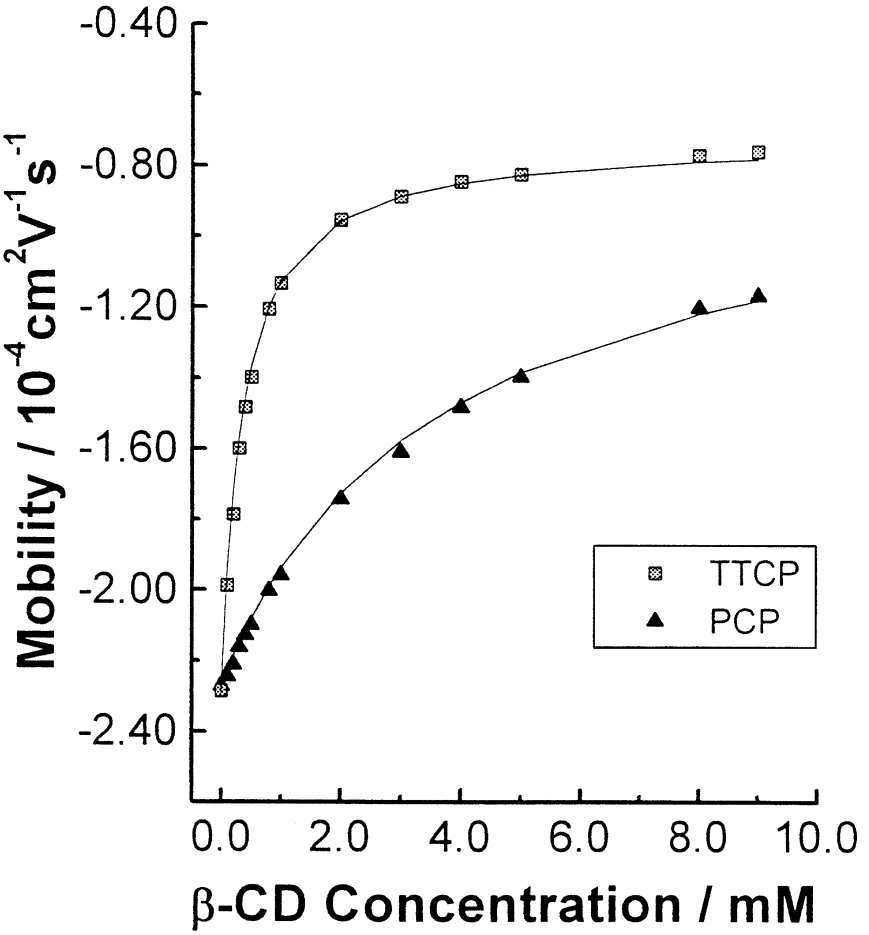

Fig. 1. The agreement between the predicted mobility curves (represented by solid lines) and experimental mobility data (shown by data points) of chlorophenols as a function of β-CD concentration: (▲), PCP; (▩), TTCP. Sample solution: chlorophenols (10 μg/ml) dissolved in a 20% methanolic aqueous solution. Buffer: phosphate buffer (70 m*M*) at pH 7.0. Capillary: 50.2 cm (effective length, 40 cm)×50 μm I.D. Detection wavelength: 215 nm. Other operating conditions: 20 kV, 25°C.

M^{-1}, respectively, with the latter being ten times larger than the former. The results clearly indicate that these two chlorophenols interact strongly with β-CD, as reflected from the variation of the electrophoretic mobility of chlorophenols shown in Fig. 1.

4.2. Electrophoretic mobility as a function of SDS concentration

4.2.1. In the absence of β-CD

Fig. 2 shows the variation of the electrophoretic mobility of chlorophenols as a function of SDS concentration in the premicellar region with chlorophenols dissolved in a 20% (v/v) methanolic solution. The observed electrophoretic mobilities are represented by the data points. The electrophoretic mobility of the two chlorophenols, migrating toward the anode, increases slightly with increasing monomeric SDS concentration from 0 to 4.5 m*M*. This is ascribed to the weak binding between the probe molecules and anionic SDS monomers. The binding constants of the two chlorophenols to anionic SDS monomers are evaluated by fitting

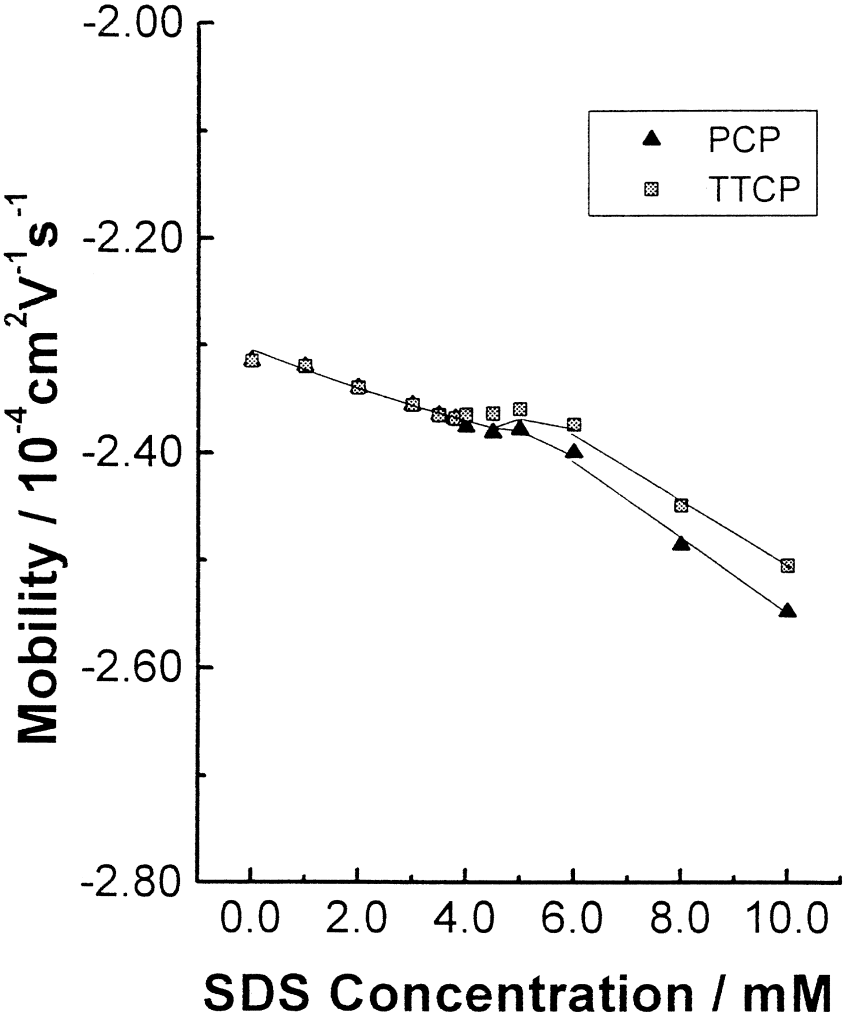

Fig. 2. The agreement between the predicted mobility curves (represented by solid lines) and experimental mobility data (shown by data points) of chlorophenols as a function of SDS concentration in the absence of β-CD: (▲), PCP; (▩), TTCP. Sample solution and operating conditions are the same as for Fig. 1.

the predicted electrophoretic mobility to the observed values using Eq. (4). The binding constants of TTCP and PCP obtained are 57 and 55 M^{-1}, respectively. These two values of binding constants are quite reasonable, judging from the variation of the electrophoretic mobility of chlorophenols shown in Fig. 2.

4.2.2. In the presence of β-CD

Fig. 3 shows the variation of the electrophoretic mobility of chlorophenols as a function of SDS concentration in the premicellar and micellar regions in the presence of β-CD at some fixed concentrations with chlorophenols dissolved in 20% (v/v) methanolic aqueous solution. As can be seen, the mobility curve of each probe molecule can be divided into two regions with two inflection points. The mobility increases (migration toward the anode) rapidly until the first inflection point is reached. Then the electrophoretic mobility of each probe molecule varies gradually with increasing the concentration of SDS monomers. This phenomenon, which is similar to the one

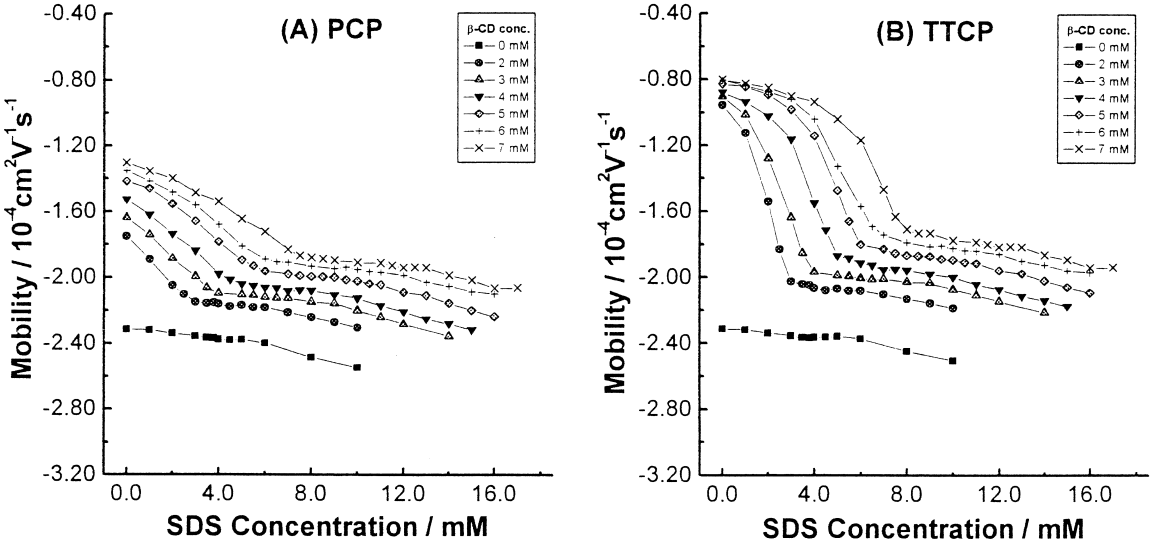

Fig. 3. Variation of electrophoretic mobility of chlorophenols as a function of SDS concentration with β-CD at some fixed concentrations in a SDS–phosphate buffer system: (A) PCP, and (B) TTCP. Operating conditions as for Fig. 1.

described in Section 4.2.1, reveals that the inclusion complexation between β-CD and anionic probe molecules becomes unfavorable in the presence of SDS, because the complexation between β-CD and SDS monomers is comparatively much stronger than that of β-CD with probe molecules. As the binding constant of β-CD to SDS reported by Wan Yunus et al. is 21 000 M^{-1} [24] and those of β-CD to TTCP and PCP evaluated in Section 4.1 are 2900 and 280 M^{-1}, respectively, β-CD molecules are expected to bind preferentially to SDS monomers, instead of binding to chlorophenols. In fact, the complexes formed between probe molecules and β-CD break up almost completely in the presence of SDS at concentrations above the first inflection point.

4.3. Prediction of electrophoretic mobility and evaluation of binding constants

For a better understanding on the stoichiometry of the complexes formed between β-CD and SDS monomers, the interactions of β-CD with probe molecules and SDS, and the influences of β-CD on the CMC value of SDS, the prediction of the effective electrophoretic mobility of probe molecules as a function of SDS concentration in the presence of β-CD is attempted. The binding constants of probe molecules to the complexes formed between β-CD and SDS, as well as that of β-CD with SDS, are evaluated. These values are determined by curve-fitting the predicted mobility data as a function of SDS concentration with the experimental mobility data through the utilization of Excel software.

The simulation of mobility curves as a function of SDS concentration in the premicellar region was carried out according to Eq. (8). The binding constants ($K_{A^-\cdot CD}$ and $K_{A^-\cdot S^-}$) and mobilities (μ_{A^-}, $\mu_{A^-\cdot CD}$ and $\mu_{A^-\cdot S^-}$) evaluated from Eqs. (2) and (4), the binding constants (K_1 and K_2) reported by Jobe et al. [36], and the mobilities of the complexes formed between probe molecules and β-CD–SDS complexes estimated according to Offord's equation [39] were all used as trial values, and the most suitable values of the binding constants and limiting mobilities of various complexes were obtained by varying these parameters and the binding constants ($K_{A^-\cdot S^-\cdot CD}$ and $K_{A^-\cdot S^-\cdot (CD)_2}$) until the predicted mobility curves were best fitted to the observed mobility curves. A typical predicted mobility curve of TTCP (dissolved in 20% methanolic aqueous solution) in the presence of 3 m*M* β-CD is shown in Fig. 4. As can be seen, the agreement between the predicted and observed mobility

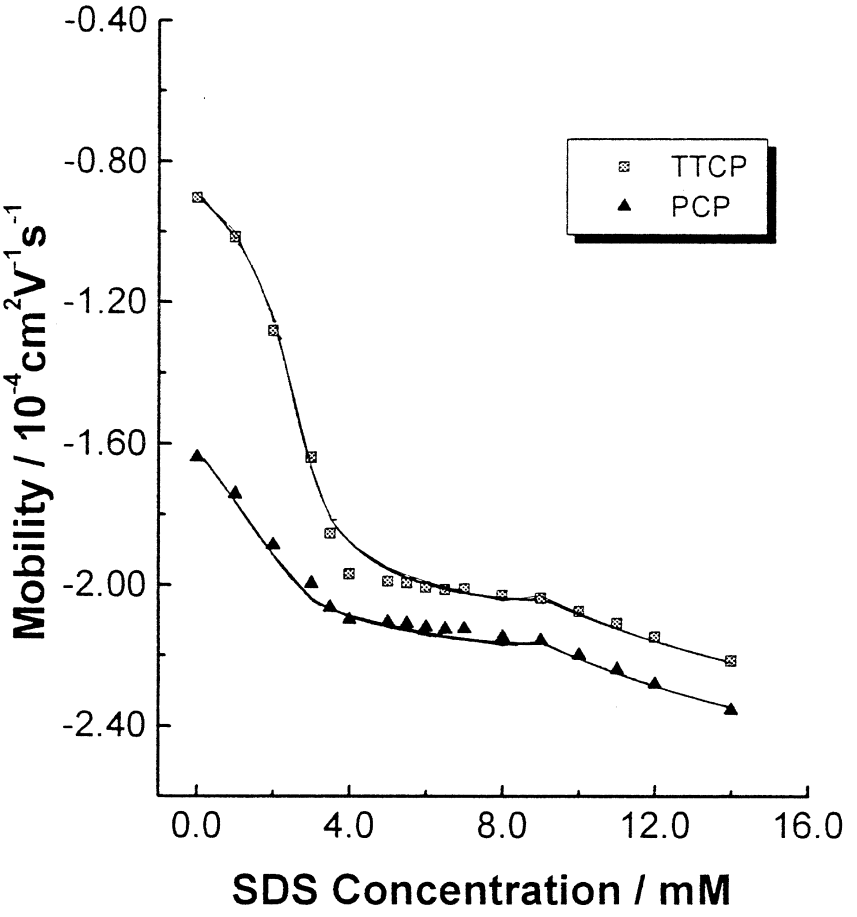

Fig. 4. The agreement between the predicted mobility curves (represented by solid lines) and experimental mobility data (denoted by data points) of TTCP as a function of SDS concentration in a SDS–phosphate buffer containing 3 m*M* β-CD. Sample solution and operating conditions as for Fig. 3.

curves is quite satisfactory. Table 1 lists the best fitted values of binding constants and mobilities of TTCP obtained. It should be pointed out here that better fitting of the mobility curve can be obtained with K_1 equal to about 48 000 M^{-1} than with K_1 equal to 21 000 M^{-1}.

A literature survey reveals that the values of binding constants for inclusion complexes involving SDS and β-CD can vary by several order of magnitude for the same system when different experimental methods are employed [26]. The K_1 values reported in the literature are: 210 [31], 356 [33], 500 [11], 1300–7230 [22], 3200–18 000 [23], 3630 [33], 8360 [25], 18 500 [40], 21 000 [24], and 25 600 [34]. The K_1 values of the complexes with a 1:1 stoichiometry reported in the literature ranging from 210 to 8360 M^{-1} are clearly unacceptable [26]. The K_1 values measured by fluorescence [34], UV and visible absorbance probes [24], and electromotive force (emf) methods involving the use of a SDS membrane selective electrode [40] give 25 600, 21 000 and 18 500 M^{-1}, respectively. These values evaluated by using three different experimental techniques are reasonably close. As the simulated mobility curves shown in Fig. 4 can yield better fitting when K_1 value greater than 21 000 M^{-1} is adapted as a parameter, the result reveals that the K_1 values ranging from 21 000 to 25 600 M^{-1} or even greater are acceptable.

Table 1
The mobility data of chlorophenols and binding constants of chlorophenols to β-CD, SDS or β-CD–SDS complexes in 70 m*M* phosphate buffer at pH 7.0

	Mobility ($\times 10^{-4}$ cm^2·V^{-1}·s^{-1})			Binding constant[a] (M^{-1})	
	TTCP	PCP		TTCP	PCP
μ_{A^-}	−2.32	−2.35	$K_{A^-\cdot CD}$	2900	280
$\mu_{A^-\cdot CD}$	−0.73	−0.75	$K_{A^-\cdot S^-}$	57	55
$\mu_{A^-\cdot S^-}$	−2.70	−2.74	$K_{S^-\cdot CD\cdot A^-}$	180	120
$\mu_{S^-\cdot CD\cdot A^-}$	−1.28	−1.30	$\frac{K_{A^-\cdot M}}{n}$	40	30
$\mu_{A^-\cdot M}$	−2.65	−2.65	$K_{S^-\cdot (CD)_2\cdot A^-}$	nil	nil

[a] $K_1 = 48\,000\ M^{-1}$; $K_2 = 210\ M^{-1}$; n, aggregation number of micelles.

4.4. Stoichiometry of β-CD–SDS complexes

As illustrated in Fig. 3, the first inflection point, which indicates the SDS concentration required to dissociate completely the complexes formed between chlorophenols and β-CD, occurs at higher SDS concentrations as β-CD concentration in the buffer solution increases. However, the mole ratios of the change in β-CD concentration (Δ[β-CD]) to the change in SDS concentration (Δ[SDS]) at these inflection points vary between 1:1.05 and 1:0.90. The result reveals that the complexes formed between β-CD and SDS exist predominantly in the form of a 1:1 stoichiometry, while the complexes with a 2:1 stoichiometry (β-CD:SDS) reported previously in the literature as a minor component may exist by less than 10%.

4.5. Influence of β-CD on CMC value of SDS

As shown in Fig. 3, the observation of a second inflection point for each mobility curve of probe molecules as a function of SDS concentration in the premicellar and micellar regions allows us to determine the CMC value of SDS. For these two probe molecules with β-CD at some fixed concentrations, the second inflection point occurs correspondingly at the higher SDS concentrations as β-CD concentration increases. The CMC values of SDS determined with β-CD at some fixed concentrations in the range 2–7 m*M* [with probe molecules dissolved in a 20% (v/v) methanolic aqueous solution] are given in Table 2. Thus the elevation of the CMC value of SDS depending on β-CD concentration in the buffer electrolyte is unambiguously evident. This is consistent with the results obtained by Junquera et al. [11] and Cifuentes et al. [17].

4.6. Influence of methanol content on the CMC of SDS

It has been demonstrated that organic solvents in the sample solution may affect the micellization of surfactant molecules [32]. As hydrophobic samples are often dissolved in a methanolic solution, it is of interest to determine the CMC values and to examine the influence of methanol content on the CMC values with such sample solutions.

Fig. 5A and B shows the variations of electrophoretic mobility of TTCP, dissolved in 5% and 30% (v/v) methanolic solutions, respectively, as a function of SDS concentration in the presence of β-CD at 3, 5, and 7 m*M*. For comparison, the variations of electrophoretic mobility of these two chlorophenols in the absence of β-CD are also included. As expected, the trends in the variation of electrophoretic mobility of chlorophenols are similar to those observed in Fig. 3B. The inflection points of the mobility curve at a given concentration of β-CD occur at relatively lower or higher concentrations of SDS than those of the corresponding mobility curve of TTCP as observed in Fig. 3B. Again, as indicated from the first inflection points, the complexes formed

Table 2
The CMC values of SDS determined in the presence of β-CD using TTCP (dissolved in 20% methanol solution) as a probe molecule and the change in mole ratio of β-CD to SDS

[β-CD]/m*M*	[SDS]/m*M* (at 1st inflection point)	Mole ratio (Δ[β-CD]/Δ[SDS])	CMC value/m*M*
2.0	3.00±0.05		7.7±0.2
		1: 0.90	
3.0	3.90±0.05		8.9±0.2
		1: 1.05	
4.0	4.95±0.05		9.9±0.2
		1: 0.90	
5.0	5.85±0.05		10.9±0.2
		1: 0.95	
6.0	6.80±0.05		11.9±0.2
		1: 0.95	
7.0	7.75±0.05		12.9±0.2

between β-CD and SDS have predominately a 1:1 stoichiometry. The CMC values of SDS determined from the second inflection points with β-CD at a concentration of 3, 5, and 7 m*M* are 7.0, 9.2 and 11.2 m*M*, respectively, for TTCP dissolved in a 5% methanolic aqueous solution and are 9.6, 11.5 and 13.5 m*M*, respectively, for TTCP dissolved in a 30% methanolic aqueous solution.

Fig. 6 shows the plots of the CMC values of SDS obtained at varied concentrations of β-CD with sample solutions containing 5%, 20% and 30% (v/v) methanol. As can be seen, three parallel straight lines are obtained and the increment of the CMC value at a particular β-CD concentration correlates well with methanol content in the sample solution. The results clearly indicate that not only β-CD concentration in the buffer electrolyte, but also methanol content in the sample solution, contributes to the elevation of the CMC value of SDS.

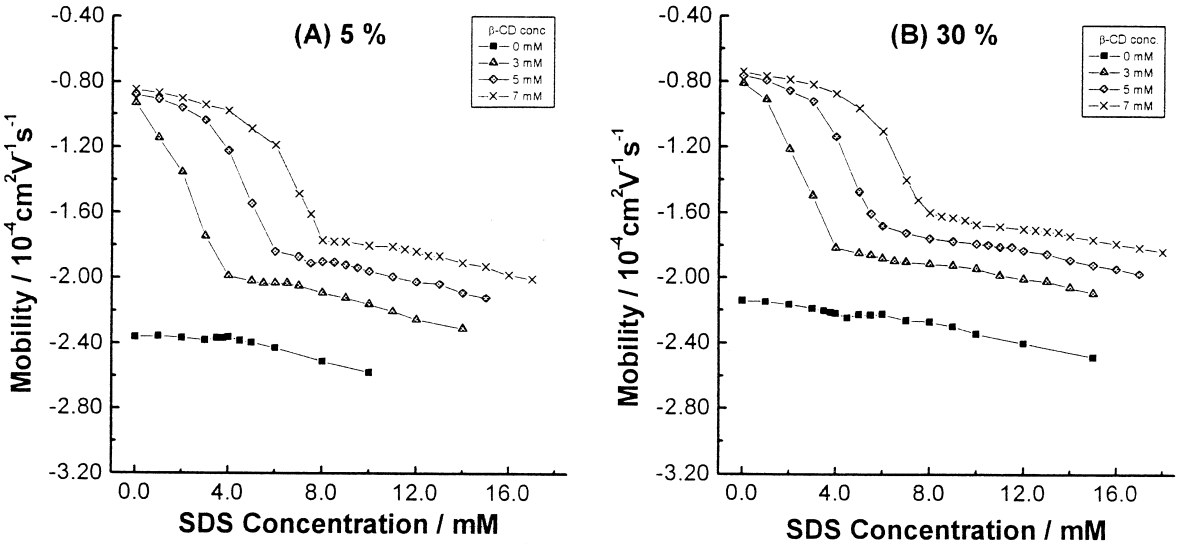

Fig. 5. Variation of electrophoretic mobility of TTCP as a function of SDS concentration with β-CD at varied concentrations in the range 0–7 m*M* obtained by dissolving probe molecules in a (A) 5% and (B) 30% methanolic aqueous solution. Operating conditions as for Fig. 3.

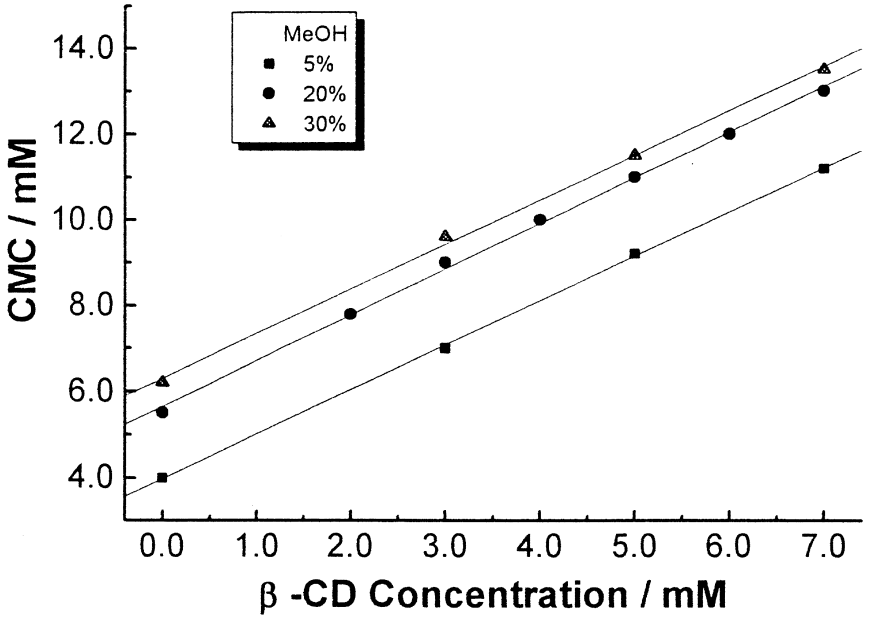

Fig. 6. Correlation of the CMC values of SDS with β-CD concentration for probe molecules dissolved in varied methanolic aqueous solutions: (■), 5%; (●), 20%; (▲), 30%.

5. Conclusion

Capillary electrophoresis is a convenient and useful technique to determine the CMC values of surfactants. With the proper choice of a probe molecule, the stoichiometry of the complexes formed between β-CD and surfactant molecules can be elucidated, and the interactions of β-CD with surfactant molecules and the influence of β-CD on the micellization of a surfactant can be better understood through the analysis of the variation of the electrophoretic mobility of a probe molecule as a function of surfactant concentration.

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