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Capillary electrophoresis study on the micellization and critical micelle concentration of sodium dodecyl sulfate Influence of solubilized solutes

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Abstract

The influence of solubilized solutes on the micellization and critical micelle concentration (CMC) of sodium dodecyl sulfate (SDS) were investigated by means of capillary electrophoresis (CE). Three different structural types of test solutes, including chloropyridines, chlorophenols and cephalosporins with different binding strength to SDS micelles, were selected in this study. The variations of the effective electrophoretic mobility of these solutes as a function of SDS concentration in the pre-micellar and micellar regions were analyzed. Interestingly, the results indicate that, in the presence of these solubilized solutes, the micellization of SDS may occur over a range of SDS concentration, with the aggregate size increasing over this range. Depending on the nature of solubilized solutes and the extent of the interactions between solubilized solutes and SDS micelles, the CMC value of SDS may vary significantly. The incorporation of solubilized solutes into SDS micelles to form mixed micelles is proposed to interpret the migration behavior of solubilized solutes in CE. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Critical micelle concentration; Micelles; Sodium dodecyl sulfate; Chloropyridines; Cephalosporins; Chlorophenol

1. Introduction

Micellar electrokinetic chromatography (MEKC) is a powerful analytical method for the separation of electrically neutral compounds [1–4]. The utilization of this separation mode of capillary electrophoretic techniques requires the addition of an ionic surfactant at a concentration above its critical micelle concentration (CMC) in a buffer solution [5]. Thus the determination of the CMC of a surfactant, particularly a new one, in a micellar buffer solution or a good knowledge of micellar properties of a surfactant is often desirable for effective MEKC separation.

A number of methods, including electrical conductivity [6–9], surface tension [10], light scattering [11,12], spectrophotometry [13–15], cyclic voltammetry [16], speed of sound [17], NMR [18], and capillary electrophoresis (CE) [19–24], have been used to determine the CMC of a surfactant. Among them, CE has proven to be a very convenient and useful technique for such a determination [20–23]. It has been shown that, by plotting the effective electrophoretic mobility of an appropriately selected test solute against surfactant concentration in the pre-micellar and micellar regions, a sharp change in slope can be observed at the CMC [20–23]. For instance, the variation of the effective electrophoretic mobility of naphthalene associated with the surfactant monomers in a borate buffer solution containing sodium dodecyl sulfate (SDS) at concentrations

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below the CMC is small, but the electrophoretic mobility varies markedly with increasing surfactant concentration above the CMC [20]. Behavior similar to that of naphthalene is observed for propazine with dodecyltrimethylammonium bromide as a cationic surfactant in a phosphate buffer solution [21].

SDS is undoubtedly the most widely used anionic surfactant in MEKC separation. The CMC value of SDS reported in the literature is 8.1–8.2 mM in pure water at 25°C [25–27], but differs from this value in a background electrolyte (BGE). In general, the CMC decreases with increasing buffer concentration or ionic strength of the BGE. For instance, the CMC value of SDS reported in the literature is 5.29 mM in 5 mM borate buffer at pH 9.2 [22] and is 4.6 mM in 10 mM phosphate–20 mM borate buffer at pH 6.8 at 25°C [28]. The CMC value can also be affected by many other factors, including buffer pH [29], temperature [29], types of buffer electrolyte [30], types of counter-ion [31], and electrolyte additives [27,28,32–37].

The addition of various electrolyte additives to the micellar buffer system has been considered to improve the selectivity and resolution of MEKC separation [28,36]. This improvement is ascribed to the modification of the micellar phase with solubilized modifiers possessing hydrophilic functional groups through specific interactions such as hydrogen bonding, the occupation of the solubilization sites in the Stern layer with the hydrophilic parts of the modifiers [28,38], or the expansion of the core volume of the micelles with the hydrocarbon parts of the modifiers [28,38].

In view of the hydrogen bond donating characteristics of SDS micelles in addition to their hydrophobic characteristics in their interior cores, it is thought that SDS micelles are accessible to solutes possessing hydrogen bond accepting characteristics [39]. Thus, the micellization of SDS is influenced when hydrophilic solutes are solubilized in the micelles, and the CMC value may significantly vary.

In this study, three different structural types of solutes, including cephadrine, cefazolin, phenol, chlorophenol, pyridine and four chloropyridines, were selected as test solutes. The influences of solubilized solutes on the micellization and the CMC of SDS were studied. Here we present the results of our investigation.

2. Experimental

2.1. Apparatus

All CE experiments were performed on a Beckman P/ACE System 5500 equipped with a UV detector for absorbance measurements. Uncoated fused-silica capillaries purchased from Polymicro Technologies (Phoenix, AZ, USA) were used. The dimensions of the capillary were 57 cm (effective length 50 cm) × 50 μm I.D. The CE system was interfaced with a microcomputer and a laser printer. SYSTEM GOLD software from 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

Pyridine and 4-chloropyridine were obtained from Tokyo Kasei Kogyo (TCL, Tokyo, Japan). 2,6-Dichloropyridine, 3,5-dichloropyridine and Sudan III were purchased from Sigma-Aldrich (St. Louis, MO, USA). 2,3,5-Trichloropyridine and SDS were supplied by Merck (Darmstadt, Germany). Phenol and 4-chlorophenol were obtained from Chem Service (West Chester, PA, USA). Cephadrine and cefazolin were purchased from Sigma (St. Louis, MO, USA). These chemicals were used as received. All other chemicals were of analytical grade. Deionized water was prepared with a Milli-Q system (Millipore, Bedford, MA, USA).

Standard solutions of test solutes at various concentrations ranging from 10 to 100 μg/ml were prepared by dissolving analytes in a methanol solution. The pH of a phosphate buffer was adjusted to 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, 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 for 30 min with 1.0 M NaOH solution,

followed by 20 min with deionized water at 25°C. Before each injection, the capillary was prewashed for 5 min with running buffer and postwashed for 2 min with deionized water, 5 min with 1.0 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 5 s under a pressure of 0.5 p.s.i. (1 p.s.i.=6894.76 Pa). The measurements were run at least in triplicate to ensure reproducibility. A voltage of 30 kV was applied. The detection wavelength was set at 214 nm for cephalosporins and 4-chlorophenol and 200 nm for chloropyridines and pyridine.

2.4. Mobility calculations

The electrophoretic mobility of analytes was calculated from the observed migration times as described previously [21].

3. Results and discussion

3.1. Theoretical consideration of electrophoretic mobility

The effective electrophoretic mobility of a neutral solute (N) both associated with the anionic surfactant monomers (S) in the pre-micellar concentration region and incorporated into the micelles in the micellar concentration region can be specifically defined by the following equations, respectively [21]:

$$\mu_{\text{eff}} = \frac{K_{\text{N}\cdot\text{S}}[\text{S}]}{1 + K_{\text{N}\cdot\text{S}}[\text{S}]} \cdot \mu_{\text{N}\cdot\text{S}} \quad (\text{below the CMC}) \quad (1)$$

and

$$\mu_{\text{eff}} = \frac{K_{\text{N}\cdot\text{S}}(\text{CMC})\mu_{\text{N}\cdot\text{S}} + K_{\text{N}\cdot\text{M}}[\text{M}]\mu_{\text{M}}}{1 + K_{\text{N}\cdot\text{S}}(\text{CMC}) + K_{\text{N}\cdot\text{M}}[\text{M}]} \quad (\text{above the CMC}) \quad (2)$$

where μ and K denote the electrophoretic mobility and binding constant, N·S represents the complexes formed between neutral analytes (N) and surfactant monomers (S), and N·M represents the complexes formed between neutral analytes (N) and surfactant micelles (M); [S] is the concentration of surfactant

monomers and [M] is the concentration of the micelles, which is defined as the total concentration of surfactant molecules minus the CMC value. As the variation of the electrophoretic mobility of a solute depends on the interaction between neutral solutes and surfactant monomers or micelles, significant variation in the electrophoretic mobility of solutes in the pre-micellar or micellar concentration region can be observed when the interaction between neutral solutes and surfactant monomers or micelles is strong. In the case of weak interactions between neutral solutes and surfactant monomers, $K_{\text{N}\cdot\text{S}}$ is small. Then μ_{eff} in Eq. (1) is equal or close to zero and Eq. (2) can be simplified as [21,40]:

$$\mu_{\text{eff}} = \frac{K_{\text{N}\cdot\text{M}}[\text{M}]\mu_{\text{M}}}{1 + K_{\text{N}\cdot\text{M}}[\text{M}]} \quad (3)$$

Accordingly, the binding constant of each individual solute to the micelles can be calculated by varying the parameters ($K_{\text{N}\cdot\text{M}}$ and μ_{M}) until the simulated mobility curve best fits the observed data, using Microsoft EXCEL. However, the mobility of micelles (μ_{M}) is usually measured experimentally using a micellar marker. Conversely, the electrophoretic mobility of each individual solute can be predicted, once the values of $K_{\text{N}\cdot\text{M}}$ and μ_{M} are known.

On the other hand, the effective electrophoretic mobility of a negatively charged solute (A^-) in the pre-micellar and micellar concentration regions, respectively can be described by the following equations [22]:

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

and

$$\mu_{\text{eff}} = \frac{\mu_{\text{A}^-} + K_{\text{A}^-\cdot\text{S}}(\text{CMC})\mu_{\text{A}^-\cdot\text{S}} + K_{\text{A}^-\cdot\text{M}}[\text{M}]\mu_{\text{M}}}{1 + K_{\text{A}^-\cdot\text{S}}(\text{CMC}) + K_{\text{A}^-\cdot\text{M}}[\text{M}]} \quad (\text{above the CMC}) \quad (5)$$

where μ_{A^-} is the electrophoretic mobility of the negatively charged solute, $K_{\text{A}^-\cdot\text{S}}$ and $\mu_{\text{A}^-\cdot\text{S}}$ are the binding constant and electrophoretic mobility, respectively, of the negatively charged solute associated with the anionic surfactant monomers, and $K_{\text{A}^-\cdot\text{M}}$ is the binding constant of the charged solutes

to the micelles. In the case of weak interactions, the term involving K_{A^-S} is small. Then Eqs. (4) and (5) can be simplified as [22]:

$$\mu_{\text{eff}} = \frac{1}{1 + K_{A^-S}[S]} \mu_{A^-} \quad (\text{below the CMC}) \quad (6)$$

or simply as $\mu_{\text{eff}} = \mu_{A^-}$, if $K_{A^-S}[S] \ll 1$ and:

$$\mu_{\text{eff}} = \frac{\mu_{A^-} + K_{A^-M}[M]\mu_M}{1 + K_{A^-M}[M]} \quad (\text{above the CMC}) \quad (7)$$

Significant variations of the electrophoretic mobility of charged solutes in the pre-micellar or micellar concentration region can be observed only when the interactions between charged solutes and surfactant monomers or micelles is strong.

Similarly, the simulation of the mobility curves of charged solutes and the evaluation of binding constants of solutes to micelles can be accomplished by performing non-linear regression with Microsoft EXCEL.

3.2. Incorporation of solubilized solutes into SDS micelles

It has been shown that the solubilization of hydrophobic probes in the SDS micelles can alter the microenvironment of probe molecules, which is reflected in the effective electrophoretic mobility of probe molecules when they are incorporated into the micelles.

3.2.1. Chloropyridines and pyridine

Fig. 1 shows the variation of the effective electrophoretic mobility of 2,3,5-trichloropyridine as a function of SDS concentration in the range 0–10 mM in a 20 mM phosphate buffer, pH 7.0. The electrophoretic mobility of this chloropyridine, migrating towards the anode, increases with increasing SDS concentration. 2,3,5-Trichloropyridine exhibits distinct variations in electrophoretic mobility over three regions of SDS concentration.

The SDS concentration at the first inflection point of the mobility curve shown in Fig. 1 is normally termed the critical aggregation concentration (CAC), at which surfactant monomers start to form aggregates

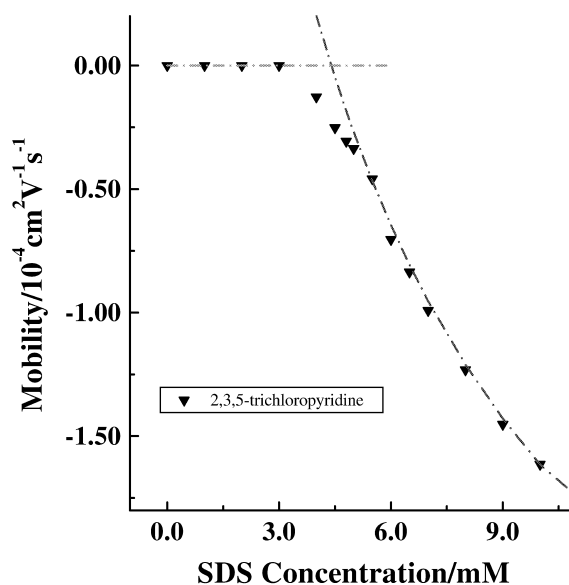


Fig. 1. Variation of the effective electrophoretic mobility of 2,3,5-trichloropyridine as a function of SDS concentration in the range 0–10 mM. Background electrolyte: 20 mM phosphate buffer, pH 7.0. Capillary: 57 cm \times 50 μm I.D. Other operating conditions: 30 kV, 25°C. Sample concentration, 15 $\mu\text{g/ml}$; sample matrix, aqueous solution containing 10% (v/v) methanol. Detection wavelength, 200 nm. The fitted mobility curves are represented by dashed lines.

gates [10,41]. The CAC value of SDS in 20 mM phosphate buffer in the presence of this chloropyridine is 3.0 mM. As the concentration of SDS increases progressively, the size of the aggregates increases until they form stable and well-defined structures. The concentration at the second inflection point of the mobility curve is called the c_2 concentration, where free micelles are present in the background electrolyte [10,41]. The c_2 concentration of SDS in the presence of 2,3,5-trichloropyridine in 20 mM phosphate is 5.2 mM. This behavior indicates that the micellization of SDS in 20 mM phosphate buffer in the presence of this chloropyridine occurs in the SDS concentration range from 3.0 to 5.2 mM. Meanwhile, 2,3,5-trichloropyridine becomes incorporated into the SDS micelles, thus causing the modification of the micellar phase.

The CMC value is greater than the CAC value but smaller than the c_2 concentration. To determine the CMC value of SDS from a curve such as in Fig. 1, it is necessary to fit this curve for both the pre-micellar

and micellar concentration regions so that the individual curve corresponding to these two concentration regions can be extended toward each other. The CMC value then occurs at the intersection of the two extrapolated mobility curves. In Fig. 1, the extrapolated mobility curve in the pre-micellar concentration region is just the line of zero mobility, because the binding constant of 2,3,5-trichloropyridine to SDS monomers, $K_{N,S}$, is very small and the effective electrophoretic mobility of this chloropyridine with phosphate buffer at low concentrations is nearly equal to zero when the SDS concentration is below the CMC. Alternatively, in Fig. 1, the electrophoretic mobility curve of 2,3,5-trichloropyridine in MEKC can be obtained by fitting it to Eq. (4) by adjusting the parameters ($K_{N,M}$, μ_M and CMC) with Microsoft EXCEL. Since μ_M can be measured experimentally using a micellar marker such as Sudan III, there is no need to adjust the value of μ_M . The fitted mobility curve of 2,3,5-trichloropyridine with SDS in the micellar concentration region is also shown in Fig. 1 by dashed line. The CMC of SDS thus determined was 4.4 mM.

Fig. 2 shows the effective electrophoretic mobility

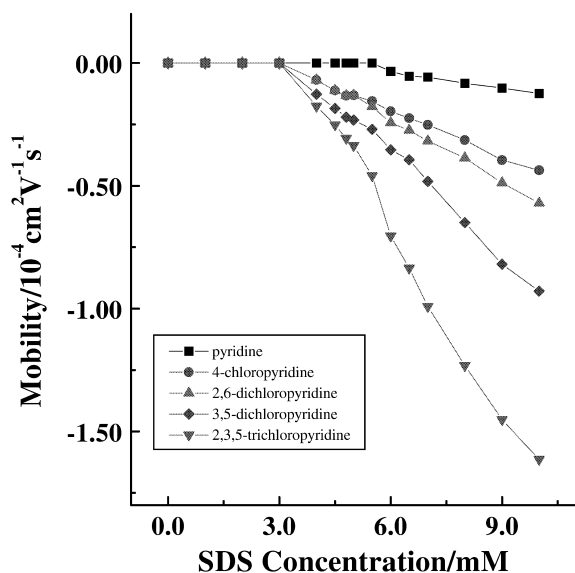


Fig. 2. Variation of the effective electrophoretic mobility of 2,6- and 3,5-dichloropyridines, 4-chloropyridine and pyridine, together with that of 2,3,5-trichloropyridine, as a function of SDS concentration in the range 0–10 mM. Operating conditions as in Fig. 1.

of two selected dichloropyridines, 4-chloropyridine, and pyridine as a function of SDS concentration in the range 0–10 mM in a 20 mM phosphate buffer, pH 7.0. For comparison, the mobility curve of 2,3,5-trichloropyridine is also included. The variations of the electrophoretic mobility of these chloropyridines are similar to those observed for 2,3,5-trichloropyridine. The three chloropyridines also exhibit distinct variation in electrophoretic mobility over three SDS concentration ranges, whereas the electrophoretic mobility of pyridine exhibits only two separate concentration dependencies. The CAC and c_2 values of SDS in the presence of these chloropyridines are listed in Table 1.

As with Fig. 1, the curve-fitted electrophoretic mobility data of these chloropyridines in the pre-micellar and micellar concentration regions of SDS were analyzed. The CMC values of SDS in the presence of these chloropyridines were determined from the intersection of the two mobility subcurves. The CMC, CAC and c_2 values of SDS in the presence of chloropyridines and pyridine, together with the binding constants of chloropyridines and pyridine to SDS micelles, are given in Table 1. The results clearly indicate that, depending on the nature of solubilized solutes, the CMC value of SDS is significantly affected by the presence of solubilized chloropyridines and that the CMC value increases with increasing binding strength between chloropyridines and SDS micelles. These results are consistent with previous findings that the addition of cyclodextrin or methanol to the SDS micellar system can lead to the formation of mixed micelles and elevate the CMC value of SDS [24,37,42–45].

The effects of buffer concentration on the micellization and the CMC of SDS were examined. The variation of the effective electrophoretic mobility of each chloropyridine as a function of SDS concentration in both 10 mM and 20 mM phosphate buffer was compared. Only one inflection point appears in the mobility curve of each chloropyridine using 10 mM phosphate buffer with sample concentration at 15 $\mu\text{g/ml}$. Also, the trends in the variations of the electrophoretic mobility of 2,3,5-trichloropyridine and 3,5-dichloropyridine are significantly different in 10 mM and 20 mM phosphate buffer. Subsequently, the binding constants of chloropyridines evaluated differ from one buffer concentration to the other. The

Table 1

Binding constants (K) of solubilized solutes to SDS micelles and the CAC, CMC and c_2 values of SDS in a micellar phosphate buffer in the presence of solubilized solutes at 25°C

Solubilized solutes	20 mM Phosphate buffer				10 mM Phosphate buffer			
	CAC (mM)	CMC (mM)	c_2 (mM)	K (M^{-1})	CAC (mM)	CMC (mM)	c_2 (mM)	K (M^{-1})
Pyridine ^a		4.8		6		6.1		6
4-Chloropyridine ^a	3.0	3.6	5.0	20		4.7		19
2,6-Dichloropyridine ^a	3.0	3.7	5.0	25		4.8		25
3,5-Dichloropyridine ^a	3.0	4.4	5.5	53		4.9		42
2,3,5-Trichloropyridine ^a	3.0	4.4	5.2	118		4.8		71
Phenol ^b		2.9		10				
4-Chlorophenol ^b	3.0	3.9	6.0	55				
Cephadrine	2.0	3.3 ^c	4.5	43 ^c	3.0	4.0 ^d	4.5	49 ^d
Cefazolin ^c	2.0	3.3		~ 0	3.0	4.5		

^a Solute concentration, 15 $\mu\text{g/ml}$.

^b Solute concentration, 10 $\mu\text{g/ml}$.

^c Solute concentration, 50 $\mu\text{g/ml}$.

^d Solute concentration, 100 $\mu\text{g/ml}$.

binding constants of 2,3,5-trichloropyridine to SDS micelles evaluated in 20 mM and 10 mM phosphate buffer are 116 and 68 M^{-1} , respectively, whereas those of 3,5-dichloropyridine are 52 and 43 M^{-1} , respectively. Apparently, the results reveal that phosphate buffer plays a significant role in the incorporation of solubilized chloropyridines into SDS micelles. Fig. 3 shows the effect of buffer concentration on the variation of electrophoretic mobility of two

representative chloropyridines (2,3,5-trichloropyridine and 2,6-dichloropyridine) as a function of SDS concentration.

Chloropyridines and pyridine exist essentially in the neutral form at pH 7.0, because the $\text{p}K_a$ values of pyridine, 4-chloropyridine and the other three chloropyridines were determined to be 4.95, 3.65 and <1.0 , respectively [40]. The binding constants of these test solutes to SDS micelles evaluated previ-

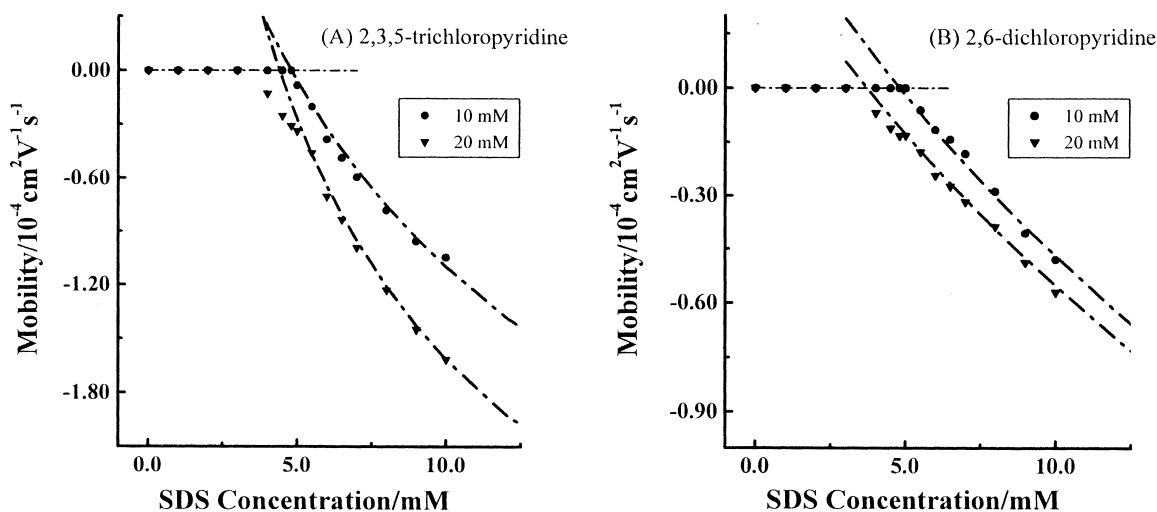


Fig. 3. Effect of buffer concentration on the variations of electrophoretic mobility of two representative chloropyridines as a function of SDS concentration in 10 mM and 20 mM phosphate buffer: (A) 2,3,5-trichloropyridine, (B) 2,6-dichloropyridine. The fitted mobility curves are shown by dashed lines and experimental results are represented as data points. Operation conditions as in Fig. 1.

ously increase in the order: pyridine < 4-chloropyridine < 2,6-dichloropyridine < 3,5-dichloropyridine < 2,3,5-trichloropyridine [40]. Combining the results of binding constants with the results obtained from Figs. 1 and 2, it shows that the extents of the variations in the electrophoretic mobility of pyridine and chloropyridines, particularly in the micellar concentration region increase in the same order as the magnitudes of the binding constants. Thus, the stronger the interaction of solubilized solutes with SDS micelles, the greater the extent of the variation in the electrophoretic mobility. The results also reveal that strong binding between chloropyridines and SDS micelles is essential in order to alter the micellar properties of a surfactant significantly.

3.2.2. 4-Chlorophenol and phenol

Fig. 4 shows the variations of the effective electrophoretic mobility of 4-chlorophenol and phenol as a function of SDS concentration in the range 0–30 mM in a 20 mM phosphate buffer, pH 7.0. Identical behavior as obtained for chloropyridines and pyridine is also observed. Two inflection points

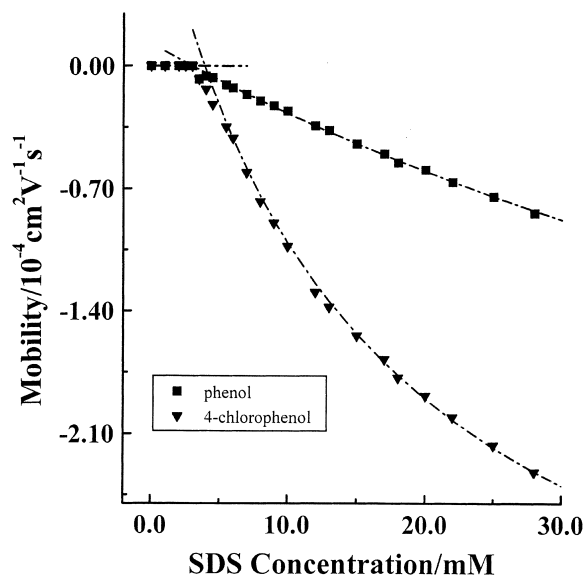


Fig. 4. Variation of the effective electrophoretic mobility of 4-chlorophenol and phenol as a function of SDS concentration in the range 0–30 mM. Detection wavelength, 214 nm. Sample concentration, 10 $\mu\text{g/ml}$. Other operating conditions as in Fig. 1. The fitted mobility curves are represented by dashed lines.

appear in the electrophoretic mobility curve of 4-chlorophenol. The CAC and c_2 values of SDS determined in the presence of 4-chlorophenol are 3.0 and 6.0 mM, respectively, and the CMC value is 3.9 mM. In the case of phenol, only one inflection point appears in the mobility curve. In this case, the CMC value which is the same as the CAC value is determined to be 3.0 mM.

3.2.3. Cephadrine and cefazolin

Cephadrine and cefazolin were also selected as test solutes. It is of interest to examine the influence of solubilized solutes on the micellization of SDS surfactant using these two cephalosporins. Cephadrine interacts rather strongly, and cefazolin very weakly with SDS micelles. Fig. 5A shows the variations of the effective electrophoretic mobility of cephadrine and cefazolin as a function of SDS concentration in the range 0–10 mM in 10 mM phosphate buffer with a solute concentration of 100 $\mu\text{g/ml}$. Phenomena similar to those obtained for chloropyridines and 4-chlorophenol are observed for cephadrine. The CAC and c_2 values of SDS in the presence of cephadrine in 10 mM phosphate buffer are 3.0 and 4.5 mM, respectively. The CMC value of SDS is 4.0 mM with cephadrine as solubilized solute.

As shown in Fig. 5A, the electrophoretic mobility of cefazolin is almost invariant with SDS micellar concentration. This fact clearly demonstrates that the interaction between cefazolin and SDS micelles is very weak. In comparison with the mobility curve of cephadrine, it is interesting to see that the micellization process of SDS is reflected in the variation of the electrophoretic mobility of cefazolin as a function of SDS concentration in the range 3.0–4.5 mM. The decrease in the electrophoretic mobility of cefazolin, migrating toward the anode, from $-1.54 \cdot 10^{-4}$ to $-1.47 \cdot 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is probably due to a progressive decrease in the net charge of the aggregates resulting from the increase in the counterion binding [45] and an increase in the mass of the aggregates as the size of the aggregates increases over this concentration range.

Fig. 5B shows the variations of the electrophoretic mobility of cephadrine and cefazolin in 20 mM phosphate buffer with the solute concentration reduced to 50 $\mu\text{g/ml}$. Phenomena similar to those

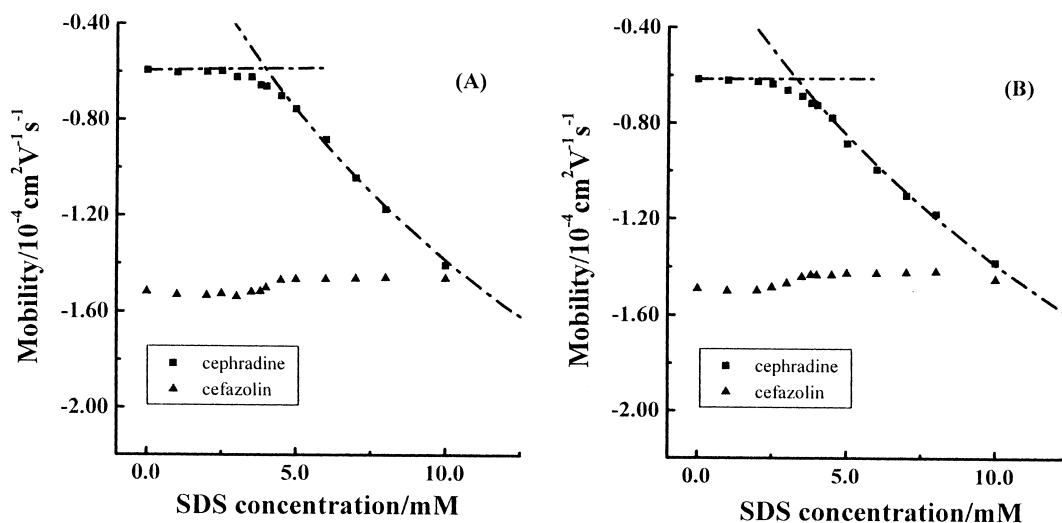


Fig. 5. Variation of the effective electrophoretic mobility of cephradine and cefazolin as a function of SDS concentration in the range 0–10 mM with varied concentrations of phosphate buffer and solute concentration: (A) buffer, 10 mM; solute, 100 µg/ml, (B) buffer, 20 mM; solute, 50 µg/ml. Other operating conditions as in Fig. 3, unless indicated. The fitted mobility curves of cephradine are represented by dashed lines.

displayed in Fig. 5A are observed. The CAC and c_2 values of SDS in the presence of cephradine are 2.0 and 4.5 mM, respectively, and the CMC is 3.3 mM. Again, the micellization of SDS is reflected in the variation of the electrophoretic mobility of cefazolin as a function of SDS over the range 2.0–3.3 mM.

With the use of phosphate buffer at low concentrations, a test solute with adequate sample concentration is required to observe the presence of two inflection points in the mobility curve. In fact, only one inflection point at 3.0 mM is observed in the mobility curve of cephradine with 20 mM phosphate buffer when the sample concentration is reduced to 10 µg/ml. On the other hand, with the use of phosphate buffer at a relatively high concentration, say 70 mM, only one inflection point is observed in the mobility curve of cephradine. The CMC value of SDS, which merges to the CAC value, decreases as buffer concentration increases.

4. Conclusion

The present investigation demonstrates that the micellization of SDS may occur in a certain concentration range of SDS and that the aggregates

increase in size over this concentration range. Depending on the nature of solubilized solutes and the interaction of solubilized solutes with the SDS micelles, the CMC value of SDS may vary over a significant range. Therefore, the influence of solubilized solutes on the CMC of a surfactant cannot be ignored, especially when solubilized solutes interact strongly with the micelles. In order to determine the CMC value of a surfactant more accurately, the electrophoretic mobility curves of solubilized solutes as a function of surfactant concentration should be carefully analyzed when using CE as a tool.

Acknowledgements

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