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Capillary zone electrophoretic separation of neutral species of chloro-*s*-triazines in the presence of cationic surfactant monomers

Ching-Erh Lin*, Ta-Zen Wang, Hui-Chun Huang, Chung-Chuan Hsueh, Yu-Chih Liu

Department of Chemistry, National Taiwan University, 1 Roosevelt Road Section 4, P.O. Box 23-34, Taipei 106, Taiwan

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Abstract

Chloro-*s*-triazines are difficult to separate by capillary zone electrophoresis (CZE), due to their low pK_a values. However, these analytes can be effectively separated by CZE in the presence of cationic surfactant monomers, such as tetradecylammonium bromide (TTAB) and dodecyltrimethylammonium bromide (DTAB). The separation mechanism based on a 1:1 binding of analytes to cationic surfactant monomers is proposed. The binding constants of chloro-*s*-triazines to cationic surfactant monomers are estimated. The results show that the strength of the interactions of these analytes with TTAB monomers is considerably strong, whereas that of the corresponding analyte with DTAB monomers is about 12- to 14-fold weaker. A linear correlation of binding constants with log P_{ow} (the logarithm of the partition coefficient of analytes between 1-octanol and aqueous phases) indicates that the migration order of these chloro-*s*-triazines depends primarily on their hydrophobicity. Moreover, the skewed peaks of chloro-*s*-triazines observed may reveal the occurrence of adsolubilization of these analytes in the adsorbed cationic surfactant layer on the capillary surface.

Keywords: Chlorotriazines; Triazines; Surfactants; Pesticides

1. Introduction

Capillary zone electrophoresis (CZE) has been successfully applied for the separation of diverse analytical samples [1–4]. The separation of analytes in CZE is often accomplished by adding electrolyte modifiers or complexing agents to the background electrolyte in order to vary the extent of chemical interactions so that the electrophoretic mobility of each individual solute can be effectively differentiated from the others.

In the normal mode of CZE separation, an electroosmotic flow (EOF) from the anode to the cathode is generated so that sample solutes can be carried to the detector. However, when the electrophoretic mobility of anionic species is close to or greater than the electroosmotic mobility, these anionic species are difficult or even unable to be detected. Under these circumstances, the use of reversed EOF is advantageous for the separation [5,6].

The reversal of the EOF is induced by adding cationic surfactants, such as long-chain alkylammonium salts, to the background electrolyte at an appropriate concentration either below the critical micelle concentration (CMC) in the case of CZE or above the CMC in the case of micellar electrokinetic

*Corresponding author. Tel.: +886-2-3691-949; fax: +886-2-3636-359.

E-mail address: celin@mail.ch.ntu.edu.tw (C.-E. Lin)

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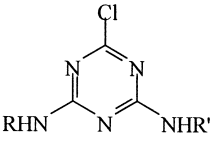
chromatography (MEKC). This is resulted from the adsorption of cationic surfactants onto the charged silica surfaces of the capillary. The adsorption occurs primarily in two successive steps [7,8]. The first step corresponds to the adsorption of individual cationic surfactant monomers by direct adsorption or ion-exchange mechanism, driven by electrostatic interactions. The second step, driven by hydrophobic interactions between the alkyl chains of oncoming surfactants and of surfactants adsorbed in the first step, corresponds to the formation of a bilayer of adsorbed surfactants or surface aggregate on the capillary wall, thus effectively making the surface charge positively [9,10]. Consequently, the electro-osmotic mobility can be varied by altering the concentration of a cationic surfactant at a particular concentration of the background electrolyte.

Chloro-*s*-triazines are important selective pre- and post-emergence herbicides used widely for the control of broadleaf and grassy weeds [11]. Because of their extensive use, toxicity, and relatively high persistence in environmental matrices [12–14], chloro-*s*-triazines are of great environmental concern. Numerous articles on the separation of *s*-triazine herbicides and their degradation products using various modes of capillary electrophoresis (CE), including CZE [15–18], isotachophoresis (ITP) [19,20], MEKC [20–24], and its hyphenated techniques [25–28], have been reported. However, the effective separation of chloro-*s*-triazines using CZE technique under the conditions of normal EOF has not been achieved [18]. This is probably due to the experimental difficulties encountered, as resulted from their low pK_a values. The pK_a values of chloro-*s*-triazines reported in the literature are in the range 1.3–2.0 [12,29–33]. Table 1 presents the pK_a values, along with log P_{ow} values (the logarithm of the partition coefficient of a solute between 1-octanol and aqueous phases) and some characteristics of chloro-*s*-triazines.

In the course of the investigation of the migration behavior and separation of *s*-triazines in MEKC using a cationic surfactant [24], we found that strong interactions were involved between chloro-*s*-triazines and tetradecyltrimethylammonium bromide (TTAB) micelles. In view of this, effective separation of chloro-*s*-triazines may be achievable by CZE in the presence of cationic surfactant monomers. Recently, an effective separation of three chloro-*s*-triazines by CZE under the conditions of reversed EOF using cetyltrimethylammonuim bromide was reported [28]. However, the separation mechanism was not discussed at all by these authors. In this paper, we report the results of our investigation on the sepa-

Table 1
Some characteristics of *s*-triazines studied



s-Triazines	Compound No.	Substituents		pK_a [a]	λ_{max} and ε_{max} [b]				Solubility [c] ($\mu g ml^{-1}$)	Log P_{ow} [d]
		R	R′		λ_1 (nm)	ε_1 ($l\ mol^{-1}\ cm^{-1}$)	λ_2 (nm)	ε_2 ($l\ mol^{-1}\ cm^{-1}$)		
Simazine	1	C_2H_5	C_2H_5	1.65	222	36 000	263	3100	5	2.26
Atrazine	2	C_2H_5	$CH(CH_3)_2$	1.68	222	41 000	263	3900	33	2.61
Propazine	3	$CH(CH_3)_2$	$CH(CH_3)_2$	1.85	221	32 000	268	3100	5	2.91
Terbuthylazine	4	C_2H_5	$C(CH_3)_3$	1.94	223	19 500	263	1500	5	3.06

[a] Refs. [12,28–32].
[b] Ref. [12].
[c] Ref. [13].
[d] Refs. [12,44].

ration of four chloro-*s*-triazines using TTAB and dodecyltrimethylammonium bromide (DTAB) as cationic surfactant monomer. The separation mechanism based on a 1:1 interaction of an analyte with cationic surfactant monomers is discussed. In addition, the binding constants of the analytes to cationic surfactant monomers are evaluated.

2. Experimental

2.1. Chemical and reagents

Of the four chloro-*s*-triazines selected in this study, terbuthylazine was purchased from Riedel-de Haen (Germany); and simazine, atrazine and propazine were supplied from Supelco (USA). TTAB and DTAB were obtained from Tokyo Kasei Kogyo (TCI, Tokyo, Japan). All other chemicals were of analytical-reagent grade. Deionized water was prepared with the Milli-Q system (Millipore, Bedford, MA, USA).

Standard solutions of chloro-*s*-triazines were prepared at a concentration ranging from 1 to 20 $\mu g ml^{-1}$ in a methanol aqueous solution containing 10% (v/v) methanol. The pH of the buffer was adjusted by mixing various proportions of 70 m*M* sodium dihydrogenphosphate buffer solution with the same concentration of disodium hydrogenphosphate solution to attain the desired value (pH 6). Methanol was used as a neutral marker.

2.2. Apparatus

Separations were made with a CE system described previously [24,34]. The dimensions of the capillary, purchased from Polymicro Technologies (Tucson, AZ, USA), were 67 cm×50 μm I.D. The UV detection position is 7.0 cm from the anodic end (the polarity of the electrodes is reversed). Sample injection was done in a hydrodynamic mode during 1 s. The CE system was interfaced with a microcomputer and a printer with software CE 1000 1.05 A. For pH measurements, a pH meter (Suntex SP-701, Taipei, Taiwan) calibrated with a precision of 0.01 pH unit was employed.

2.3. Electrophoretic procedure

When a new capillary was used, the capillary was washed using a standard sequence described previously [34]: that is, 10 min with deionized water at 60°C, 60 min with 1.0 *M* NaOH at 60°C and then 10 min with deionized water at 25°C. To ensure reproducibility, all experiments were performed at 25°C and measurements were run at least in triplicate. The capillary was pre-washed for 5 min with running buffer before each injection and post-washed for 10 min with deionized water at 25°C, followed with 1.0 *M* sodium hydroxide solution at 25°C for 5 min and with 0.1 *M* sodium hydroxide solution at 25°C for 5 min, and then with deionized water at 25°C for 5 min to maintain proper reproducibility for run-to-run injections. The detection wavelength was set at 220 nm. The signs of the electroosmotic and electrophoretic mobilities are defined such that the direction of the migration from anode to cathode is positive.

2.4. Calculation of electrophoretic mobility

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

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

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.

3. Results and discussion

3.1. Electrophoretic mobility as a function of the concentration of surfactant monomers

Fig. 1 depicts the schematic diagram of the migration of a neutral solute associated with cationic surfactant monomers in CZE. The effective electro-

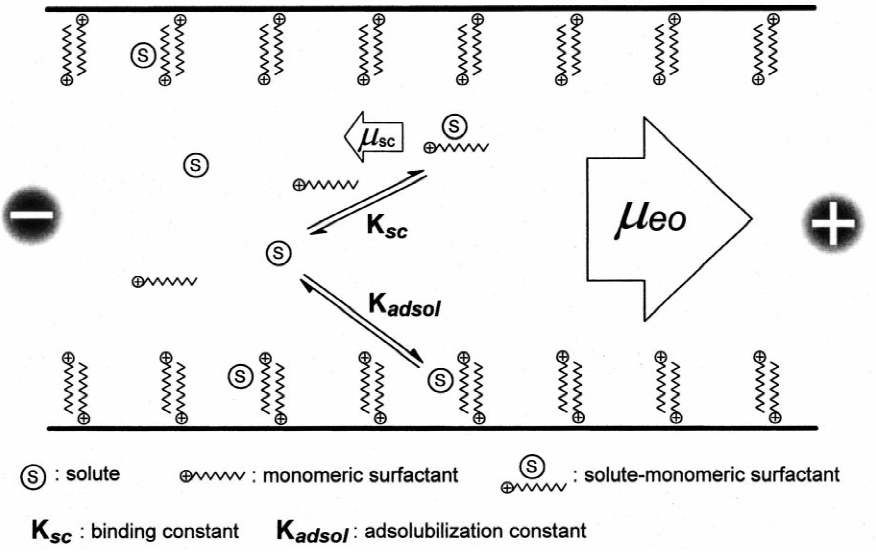


Fig. 1. Schematic diagram of the migration of a neutral solute associated with cationic surfactant monomers in CZE.

phoretic mobility of a neutral solute in CZE can be expressed as:

$$\mu_{\text{eff}} = \alpha_{\text{sc}}\mu_{\text{sc}} \quad (2)$$

where α_{sc} and μ_{sc} are the mole fraction and limiting electrophoretic mobility of the solute associated with surfactant monomers in the aqueous phase, respectively. When cationic surfactant monomers are used as complexing agents, the electrophoretic process involves the following equilibrium between an analyte (A) and surfactant monomers (S),

$$\text{A} + \text{S} \overset{K_{\text{sc}}}{\rightleftharpoons} \text{A}\cdot\text{S}$$

where K_{sc} is the binding constant of a solute to surfactant monomers. The mole fraction (α_{sc}) can be expressed in terms of K_{sc} and [S] as [35–37]:

$$\alpha_{\text{sc}} = \frac{K_{\text{sc}}[\text{S}]}{1 + K_{\text{sc}}[\text{S}]}$$

where [S] is the concentration of surfactant monomers and is defined as:

$$[\text{S}] = \frac{[\text{S}]_{\text{T}}}{1 + K_{\text{sc}}[\text{A}]}$$

where [A] is the analyte concentration and $[\text{S}]_{\text{T}}$ is the total concentration of surfactant monomers which is less than the CMC of the surfactant. Thus, the electrophoretic mobility of a solute can specifically be defined by the following equation [35–37]:

$$\mu_{\text{eff}} = \frac{K_{\text{sc}}[\text{S}]\mu_{\text{sc}}}{1 + K_{\text{sc}}[\text{S}]} \quad (3)$$

The CMC values of TTAB and DTAB determined in a phosphate buffer (70 m*M*) at pH 6.0 are 1.6±0.1 and 11.0±0.2 m*M*, respectively [38]; the CMC values of DTAB determined in pure water and in a phosphate buffer (20 m*M*) at pH 6.0 are 15.6 [8] and 12.4 m*M* [39], respectively. Therefore, the concentration of TTAB and DTAB monomers added to the phosphate buffer should be less than 1.6 and 11.0 m*M*, respectively. Fig. 2 shows the effective electrophoretic mobility of four chloro-*s*-triazines (indicated by the data points) obtained in a phosphate buffer at pH 6.0 with TTAB and DTAB concentrations varying in the range 0.6–1.6 and 4.0–10.0 m*M*, respectively. As expected, the mobility of each individual chloro-*s*-triazines increased with increasing surfactant concentration. According to Eq. (3), the migration behavior of these chloro-*s*-triazines is quantitatively predictable, provided that the binding constant and limiting electrophoretic mobility of the complexes formed between *s*-triazines and surfactant monomers are known.

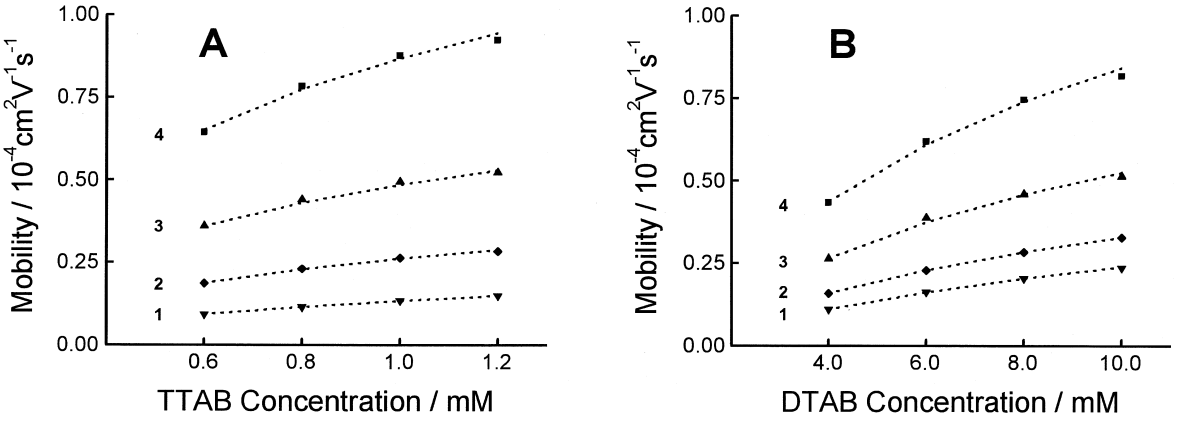


Fig. 2. The variation of observed (indicated by data points) and predicted (represented by dotted lines) electrophoretic mobility curves of chloro-*s*-triazines as a function of the concentration of surfactant monomers (with corrected total surfactant concentration): (A) TTAB, (B) DTAB. Capillary: 67 cm×50 μm, I.D. Buffer: 70 m*M* phosphate buffer at pH 6.0. Other operating conditions: −15 kV, 25°C. Solute: 1=simazine, 2=atrazine, 3=propazine, 4=terbuthylazine.

3.2. Determination of K_{sc} and μ_{sc} values of chloro-s-triazines

The values of K_{sc} and μ_{sc} can be determined either by linear-plot method or by curve-fitting method. In the former case, Eq. (3) can be rearranged and expressed as:

$$\frac{1}{\mu_{eff}} = \frac{1}{\mu_{sc}} + \frac{1}{\mu_{sc}K_{sc}[S]} \quad (4)$$

By plotting $1/\mu_{eff}$ vs. $1/[S]$, the values of K_{sc} and μ_{sc} can be estimated from the slope and intercept of a straight line obtained. The values of K_{sc} and μ_{sc} estimated by the linear-plot method without the correction of total surfactant concentration (assuming that the adsorption of surfactant monomers onto the capillary surfactant does not take place in the electrophoretic process) are listed as the numbers in parentheses in Table 2.

In the curve-fitting treatment, the electrophoretic mobility curves of chloro-*s*-triazines based on Eq. (3) were simulated using Excel software. The binding constants (K_{sc}) and limiting mobility (μ_{sc}) of each individual solute evaluated from the linear-plot method were used as trial values. The most suitable values of K_{sc} and μ_{sc} were then obtained by varying these parameters until the predicted mobility curves were best-fitted to the observed mobility curves. The values of K_{sc} and μ_{sc} evaluated by curve-fitting method without the correction of total surfactant concentration are listed as the numbers in parentheses in Table 3. It should be noted that the agreement between the predicted and observed mobility curves

Table 2
The binding constants and mobility data of chloro-*s*-triazines evaluated by linear-plot method[a]

Chloro-*s*-triazine	Binding constant (M^{-1})		Mobility (10^{-4} cm^2 V^{-1} s^{-1})	
	TTAB	DTAB	TTAB	DTAB
Simazine	877 (546)	69 (25)	0.31 (0.39)	0.62 (1.21)
Atrazine	1176 (773)	86 (37)	0.53 (0.62)	0.75 (1.23)
Propazine	1533 (1039)	105 (51)	0.88 (1.00)	1.08 (1.59)
Terbuthylazine	1642 (1120)	117 (60)	1.53 (1.72)	1.65 (2.30)

[a] The numbers are evaluated with corrected total surfactant concentration by assuming $[S]_{ads}$ equal to 0.085 m*M* for TTAB and 0.85 m*M* for DTAB; the numbers in parentheses are evaluated without correction ($[S]_{ads}=0$).

Table 3
The binding constants and mobility data of chloro-*s*-triazines evaluated by curve-fitting method[a]

Chloro-*s*-triazine	Binding constant (M^{-1})		Mobility (10^{-4} cm^2 V^{-1} s^{-1})	
	TTAB	DTAB	TTAB	DTAB
Simazine	885 (543)	69 (26)	0.31 (0.39)	0.62 (1.18)
Atrazine	1174 (765)	86 (37)	0.53 (0.62)	0.75 (1.23)
Propazine	1525 (1030)	106 (51)	0.88 (1.00)	1.08 (1.56)
Terbuthylazine	1640 (1125)	115 (59)	1.53 (1.70)	1.65 (2.30)

[a] The numbers are evaluated with corrected total surfactant concentration by assuming $[S]_{ads}$ equal to 0.085 m*M* for TTAB and 0.85 m*M* for DTAB; the numbers in parentheses are evaluated without correction ($[S]_{ads}=0$).

is satisfactory for most of the surfactant–analyte complexes, except DTAB–terbuthylazine, DTAB–propazine and TTAB–terbuthylazine complexes. Unfortunately, as indicated in Tables 2 and 3, the electrophoretic mobility of surfactant–analyte complexes, particularly, those of DTAB–analyte, are probably overevaluated. Thus, the binding constants of DTAB–analyte complexes calculated are too small, whereas the values evaluated for TTAB–analyte complexes are too large.

In order to improve the agreement between the predicted and experimental mobility curves of surfactant–analyte complexes and to obtain reasonable values of μ_{sc} of surfactant–analyte complexes, especially those of DTAB–analyte complexes, the correction of total surfactant concentration is necessary. This is done by subtracting the amount of surfactant monomers which are adsorbed onto the capillary surface in the process of electrophoretic separation from the total surfactant concentration. That is, the corrected total surfactant concentration is defined as the total concentration of surfactant monomers ($[S]_T$) minus the concentration of adsorbed surfactant monomers ($[S]_{ads}$).

The values of μ_{sc} of surfactant–analyte complexes decrease with increasing the concentration of adsorbed surfactant monomers. With $[S]_{ads}=0.1$ m*M* for TTAB and $[S]_{ads}=1.0$ m*M* for DTAB, the limiting electrophoretic mobility of TTAB–terbuthylazine complex is nearly equal to that of DTAB–terbuthylazine complex. As the electrophoretic mobility of TTAB–analyte complex should be smaller than that of the corresponding DTAB–analyte complex, the concentration of adsorbed surfactant monomers should not exceed 0.1 m*M* for TTAB–analyte complexes and should be less than 1.0 m*M* for DTAB–analyte complexes.

The concentration of adsorbed surfactant monomers is determined by assuming that the ratio of the electrophoretic mobility of DTAB–terbuthylazine complex to that of TTAB–terbuthylazine complex is equal to the ratio of the electrophoretic mobility of DTAB to that of TTAB, which is 1.08. In the present study, the adsorbed surfactant concentration ($[S]_{ads}$) is estimated to be about 0.085 m*M* for TTAB and about 0.85 m*M* for DTAB. The binding constants (K_{sc}) and the mobility (μ_{sc}) are then determined either by linear-plot method according to Eq. (4) or by curve-fitting method based on Eq. (3). The values of K_{sc} and μ_{sc} determined by linear-plot method are listed in Table 2 and these evaluated by curve-fitting method are given in Table 3. As shown in Fig. 2, the agreement between the predicted mobility curve (represented by dotted line) and the experimental mobility curve (indicated by data point) for each individual analyte, even for DTAB–terbuthylazine complex, is very good. The results also indicate that the strength of the interactions of these analytes with TTAB surfactant monomers is considerably strong, whereas that of the corresponding analyte with DTAB monomers is about 12- to 14-fold weaker. The binding constants of chloro-*s*-triazines to surfactant monomers increase in the order simazine$<$atrazine$<$propazine$<$terbuthylazine, as reflected from the extent of the variation in the effective electrophoretic mobility as a function of the concentration of surfactant monomers shown in Fig. 2.

3.3. Capillary zone electrophoretic separation of neutral species in the presence of cationic surfactant monomers

Two typical electropherograms of chloro-*s*-triazines obtained with a phosphate buffer (70 m*M*)

containing 1.0 m*M* TTAB and 8.0 m*M* DTAB, respectively, at pH 6.0 are shown in Fig. 3A and 3B. As demonstrated, complete separations of chloro-*s*-triazines in CZE were achieved in the presence of cationic surfactant monomers at a concentration below their critical micelle concentrations.

It is noteworthy that, as indicated by the magnitudes of the binding constants, the migration of these analytes follows the order simazine<atrazine<propazine<terbuthylazine. The binding constants of these analytes to TTAB and DTAB monomers evaluated with or without correction in total surfactant concentration are well correlated with log P_{ow}. The correlation coefficients (r^2) for the TTAB– and DTAB–analyte complexes with correction in total surfactant concentration are equal to 0.9970 and 0.99686, respectively. As the value of log P_{ow} is an index of the hydrophobicity of the solute, the results clearly indicate that the migration order of these chloro-*s*-triazines is primarily determined by their hydrophobicity.

3.4. Adsolubilization of chloro-s-triazine analytes

It is well known that the adsorption mechanism of cationic surfactants primarily involves two steps

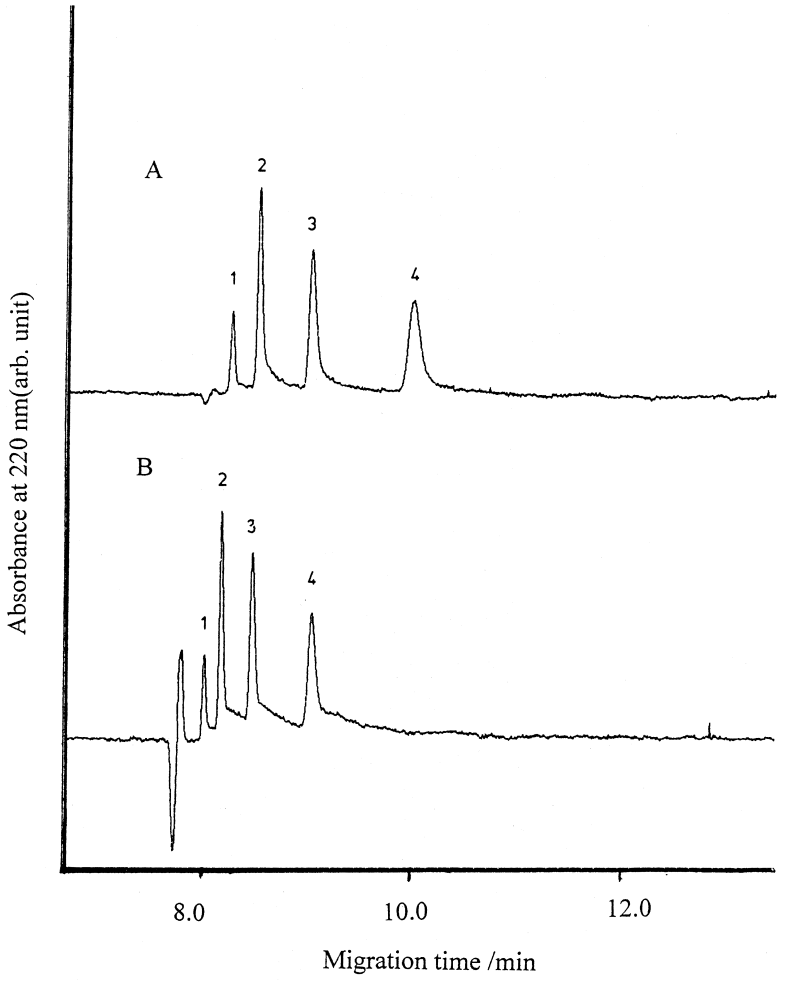


Fig. 3. Typical electropherograms of chloro-*s*-triazines obtained with addition of cationic surfactant monomers: (A) 1.0 m*M* TTAB; (B) 8.0 m*M* DTAB. Peak identification as in Fig. 2.

[7,8,40–42]. The first adsorption step corresponds to the adsorption of individual surfactant ions on the negative sites of the silica surface, driven by electrostatic interactions and the second adsorption step is driven by hydrophobic interactions between surfactant alkyl chains and is resulted in the formation of a bilayer of cationic surfactants or surface aggregates [7,8,40,43]. The adsorbed layer of cationic surfactants formed on the capillary surface provides hydrophobic circumstances which can incorporate hydrophobic compounds [7]. This phenomenon is refereed to as ''adsolubilization'' [7,38,41]. Moreover, surfactant adsorption on the surface is shown to continue even after the CMC is reached [8]. Thus after the adsorption of cationic surfactants on the capillary surface, a two-step process of adsorption–adsolubilization occurs for hydrophobic compounds and the analytes are partitioning between the adsolubilized surfactants and the aqueous phase containing surfactant monomers or micelles. For example, adsolubilization of 2-naphthol in the bilayer of the adsorbed dodecyltrimethylammonium chloride on the silica surface was reported [7]. The amount of adsolubilized analytes increases, reached a maximum, then decreases with increasing the concentration of cationic surfactants. Based on a similar argument, the adsolubilization of chloro-*s*-triazines is very likely to occur during the electrophoretic process. As shown in Fig. 3, the peak shape of chloro-*s*-triazines is somewhat skewed with TTAB surfactant monomers and is deteriorated to a greater extent with DTAB surfactant monomer at pH 6.0. The results suggest the occurrence of adsolubilization of chloro-*s*-triazines in the adsorbed bilayer of cationic surfactants on the capillary surface. The deterioration of peak shape can be improved by increasing the concentration of cationic surfactants or decreasing the content of methanol in the buffer solution so that the amount of adsolubilized analytes can be reduced. However, within the framework of CZE separation, the concentration of cationic surfactants is restricted to a value below the CMC. Thus the improvement of the peak shape of analytes is more or less limited and a symmetrical peak shape without tailing seems to be very difficult to obtain for analytes separated by CZE with cationic surfactants. Also, it should be noted that, as the analytes are in the neutral form, the separation of chloro-*s*-triazines is not effected by adsolubilization alone.

4. Conclusion

Complete separations of neutral species of chloro-*s*-triazines by CZE using cationic surfactant monomers as electrolyte modifier were achieved. The separation mechanism mainly based on a 1:1 interaction of analytes with cationic surfactant monomers is proposed. The migration order of these chloro-*s*-triazines is primarily determined by their hydrophobicity. Adsolubilization of these analytes is very likely to occur in the adsorbed bilayer of cationic surfactants. Adsolubilization can affect the asymmetry of the peak shape. However, adsolubilization alone is not effective enough to separate neutral species of chloro-*s*-triazines.

Acknowledgements

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