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Simultaneous control of electrostatic micellar partition and electroosmotic flow-rate by anion-dominated partition into zwitterionic micelles

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Abstract

The zeta potentials of zwitterionic micelles and capillary walls have been evaluated with capillary electrophoresis. The zeta potential of the micelles is predominantly determined by the nature of anions, while cations of identical valence have marginal effects; the linear relation has been found between the induced zeta potential and the hydration energy of an anion. The zeta potential of the capillary wall is also varied with anionic natures, and there is a good correlation between micellar and capillary wall zeta potential. This strongly suggests that the zeta potential of capillary walls is determined by the partition of anions into the surfactant layer formed on the capillary wall. Thus, we can simultaneously control both the electroosmotic flow-rate and micellar surface potential (in turn electrostatic interaction between micelles and ionic solutes) by varying the type and concentration of electrolytes. This idea has been applied to the separation of aromatic cationic solutes.

Keywords: Zeta potential; Charge density; Micelles

1. Introduction

Capillary electrophoresis (CE) is an effective tool not only for separation of a variety of compounds but also for the evaluation of electrokinetic phenomena. Electrophoresis and electroosmosis are typical electrokinetic phenomena involved in CE, and are directly related to the performance of CE separation. The resolution (R_s) between two closely migrating solutes is given by:

$$R_s = \frac{\mu_1 - \mu_2}{4\sqrt{2}} \cdot \sqrt{\frac{V}{D(\bar{\mu} + \mu_{eo})}} \quad (1)$$

where μ_1, μ_2, $\bar{\mu}$, and μ_{eo} are the electrophoretic mobility of solute 1, that of solute 2, their mean mobility, and the mobility of an electroosmotic flow, V and D are the applied voltage and the diffusion coefficient of the solutes [1]. Eq. (1) clearly indicates that $(\mu_1 - \mu_2)$ should be enlarged and/or $(\bar{\mu} + \mu_{eo})$ should be reduced for better separation. The electrophoretic mobility of solutes may be altered through their equilibria in solution and the ionic strength of running electrolytes; an appropriate separation condition to allow large differences in $(\mu_1 - \mu_2)$ is thus sought by varying these parameters. On the other hand, smaller $(\bar{\mu} + \mu_{eo})$ is usually attained by adjusting μ_{eo}. A number of researchers have focused on the control of electroosmosis to optimize resolution of their interest [2–6]. Coating capillary inner walls is one of the common ways to manipulate electroosmosis [2–4].

In a micellar electrokinetic chromatographic

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(MEKC) mode, the electrophoresis of micelles employed in running solutions is another important factor to govern separation. The migration rates of non-ionic solutes should be intermediate between those of a micelle and of an electroosmotic flow, meaning that the width of a separation window depends on these two parameters, i.e. the electrophoretic mobility of the micelle and the electroosmotic flow-rate. Although the charge density of micelles is not a very important factor to determine the interaction between micelles and non-ionic solutes, the electrostatic character of ionic micelles plays a decisive role in the partition of ionic solutes. Mixed micelles have been, for example, studied for the relaxation of electrostatic interaction between ionic solutes and ionic micelles [7]. Thus, controlling both an electroosmotic flow-rate and the electrostatic interaction of solutes with micelles is feasible by changing either the type or the nature of surfactants.

In the present work, we focus our attention on the electrostatic characteristics of zwitterionic dodecyldimethylammoniopropanesulfonic acid (DDAPS) micelles. The DDAPS molecule bearing an anionic and cationic group has no net charges, and, in turn, the DDAPS micelles also have no charges if they are present in water. However, in an electrolyte, the imbalance between anion- and cation-partition induces surface charges and surface potential [8–10]. Although zwitterionic micelles have been employed as carriers in micellar electrokinetic chromatography and as electroosmotic flow modifiers in CE [3,11,12], no attempts have been made to understand the electrostatic features of zwitterionic micelles on the basis of the relation between induced potential and the nature of electrolytes. We determine the surface potentials of the DDAPS micelles and the capillary wall adsorbing DDAPS molecules in various electrolytes, and optimize separation of aromatic compounds on the basis of the partition and electrostatic natures of DDAPS.

2. Experimental

The capillary electrophoretic system was composed of a Matsusada Precision Devices high-voltage power supply Model HCZE-30P No.25, a JASCO UV–Visible detector Model 870-CE and a fused-silica capillary (60 cm×50 μm I.D.). Currents ranged from 10 to 70 μA, depending on the concentration and the nature of a running electrolyte, under a 12 kV applied voltage. Sample solutions were introduced from the anodic end by siphoning. The CE system was set in a thermostated incubator to keep temperature constant at 25°C. Unless otherwise stated, sodium salts were used as electrolytes.

DDAPS was purchased from Tokyo Kasei, and recrystallized from methanol–acetone twice. Other reagents were of analytical grade. Solutions were prepared in distilled deionized water.

3. Results and discussion

3.1. Determination of the zeta potential of DDAPS micelles

The mobility of a micelle (μ) under a given condition is represented by:

$$\mu = \frac{L}{E} \cdot \left(\frac{1}{t_{\mathrm{app}}} - \frac{1}{t_{\mathrm{eo}}} \right) \tag{2}$$

where E is the applied electric field strength, L is the effective length of the capillary (the length between the injection end and the detection window), and t_{app} and t_{eo} are the migration times of the micelle and the electroosmotic flow. When the zeta potential is not very high, the following Henry's equation is applicable to the determination of the zeta potential (ζ_{m}) of the micelle [13]:

$$\mu = \frac{\epsilon_0 \epsilon \zeta_{\mathrm{m}}}{\eta} \cdot f(\kappa a) \tag{3}$$

where η is the viscosity of a medium and $f(\kappa a)$ is Henry's coefficient, κ and a are the Debye shielding parameter and the radius of the micelle. We can thus determine the zeta potential of the micelle from μ. In the present study, the electrophoresis of the DDAPS micelles was detected by monitoring the migration of pyrene solubilized in the micelles.

The resolution between the DDAPS micelles and electroosmotic flow marker (acetone) is given by substituting $\mu_1 = 0$ into Eq. (1). R_{s} should be larger than unity for baseline separation when the intensities of adjacent peaks are almost identical. However, $R_{\mathrm{s}} = 0.5$ will be large enough to evaluate the

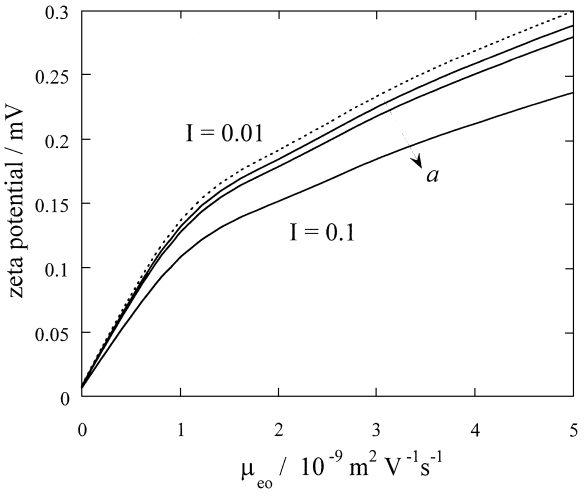

Fig. 1. Changes in the detectable zeta potential of micelles with μ_{eo}. Solid curves, $I=0.1$ *M*, and $a=1.6$, 2.0, and 2.4 nm. Dotted curve, $I=0.01$ *M* and $a=2$ nm. Detectable zeta potential was estimated by assuming $R_s=0.5$.

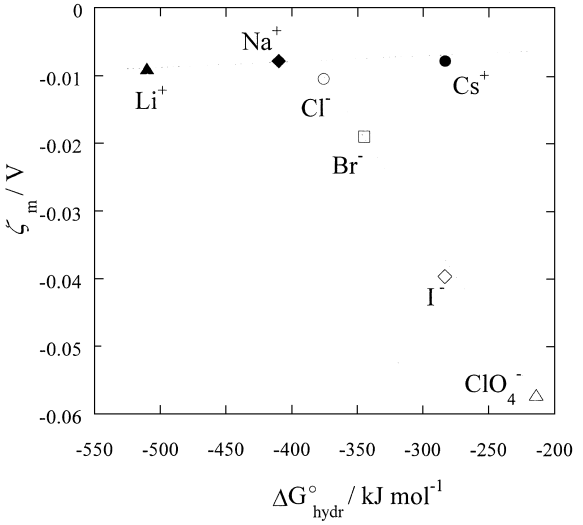

Fig. 2. Relation between ζ_m and the hydration energies of ions. ζ_m was determined in 50 m*M* electrolytes. Na^+ salts were used for studying an anion effect, and Cl^- salts were used for a cation effect.

zeta potential (peak separation is necessary, but baseline separation is not necessary). Fig. 1 shows the zeta potential that is detectable by CE, where the zeta potential estimated for various systems by assuming $R_s=0.5$ is plotted against μ_{eo}. This figure clearly indicates that the smaller μ_{eo} is preferable for detection of smaller zeta potentials. As can be seen in Eq. (3), Henry's coefficient is a function of the Debye shielding parameter and the radius of a micelle. Micellar radii typically range from 1.5 to 3 nm, e.g. *a* for DDAPS micelle is reported to be 2.6 nm [10], for hexadecyltrimethylammonium chloride 2.17 nm [13], for sodium dodecylsulfate (SDS) 1.67 nm [14]. Fig. 1 illustrates the results calculated for $a=1.6$, 2.0, and 2.4 nm at $I=0.01$ *M* and 0.1 *M*. The detectable zeta potential is a function of *a* at ionic strength $I=0.1$ *M*, while its effect is negligible in solutions of low ionic strength. CE can detect smaller surface potential for larger micelles. By adjusting μ_{eo}, it is possible to detect zeta potentials smaller than 0.1 mV. This very high detectability is an advantage of CE in this application.

As previously reported, the zeta potential of the DDAPS micelles depends on the nature of electrolytes [8,9]. Cation effects are negligible as far as their charges are identical. In contrast, anions play critical roles in determination of the surface potential of the DDAPS micelles. Fig. 2 shows the relation between the hydration energies of ions and the zeta potential of the DDAPS micelles induced in 50 m*M* salt solutions [15]. The zeta potential decreased with decreasing concentration of electrolytes, though not shown. Fig. 2 clearly indicates that the zeta potential of the DDAPS micelles depends on the hydration natures of anions, while the cationic effect is marginal. This characteristic behavior of the DDAPS micelles is partly due to the polarity of the DDAPS molecule, and mostly due to a difference in hydration natures between cations and anions; cations form rather clear hydration shells, but anions do not.

3.2. The zeta potential of the capillary wall

The DDAPS molecules are adsorbed on the capillary wall, and allow the modification of electroosmotic flow-rates. Similar strategies, i.e. use of coated capillaries, are often employed to modify electroosmotic flow-rates, it is an efficient feature of the present case that the modification is possible by varying types of electrolytes (not the type of a surfactant). Fig. 3A shows the zeta potentials of the capillary wall in various electrolytes containing 50 m*M* DDAPS. The zeta potential of the capillary wall

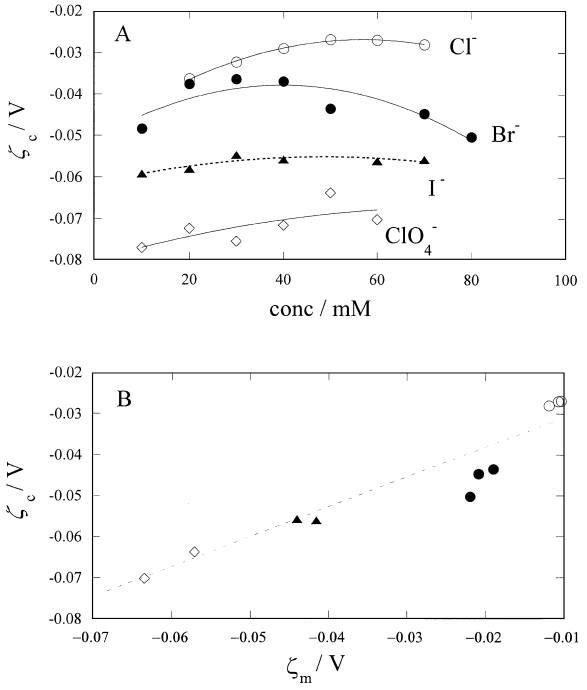

Fig. 3. (A) Changes in ζ_c with the concentration of a salt and (B) relation between ζ_c and ζ_m. Curves are for eye guide. (B) The data obtained with solution of >50 m*M* were plotted, and symbols are the same as in (A).

(ζ_c) was calculated based on the Helmholtz–Smoluchowski equation [13]:

$$\mu_{eo} = \frac{\epsilon_0 \epsilon E \zeta_c}{\eta} \quad (4)$$

The zeta potential becomes more negative in the order of $Cl^- < Br^- < I^- < ClO_4^-$; this order is the same as that of decreasing zeta potential of the DDAPS micelles. The zeta potential of the capillary wall shows a maximum when varying electrolyte concentrations. When the charge density of the capillary wall is constant (e.g. in cases of ionic surfactant solutions), the zeta potential becomes smaller when increasing ionic strength due to electrical double layer shrinking. However, in the present case, increasing ionic strength causes an increase in the negative charge density by anion-dominated partition to the DDAPS layer. Thus, these opposite trends are superimposed, and produce maxima at intermediate concentration ranges. The correlation between micellar and capillary wall zeta potentials is shown in Fig. 3B, where results obtained with electrolytes of ≥50 m*M* are plotted to highlight partition effects on the zeta potential. There is a very good correlation between them, strongly suggesting that the anion-dominated partition to the DDAPS layer governs the electroosmotic flow-rates as well as the electrophoresis of the DDAPS micelles. This result agrees with our previous chromatographic study of ionic partition to zwitterionic surfaces [16].

The pH of a running buffer is another important factor to determine electroosmotic flow-rates. At pH 2, the direction of electroosmotic flow was the same as at pH 9 (anode to cathode), but its magnitude significantly decreased by the reduced dissociation of surface silanol groups; ζ_c at pH=2 was −44.8 mV (−63.7 mV at pH 9) in 50 m*M* ClO_4^- solution and 10.1 mV (−26.8 mV at pH 9) in 50 m*M* Cl^- solution. It should be noted that, even in an acidic solution,

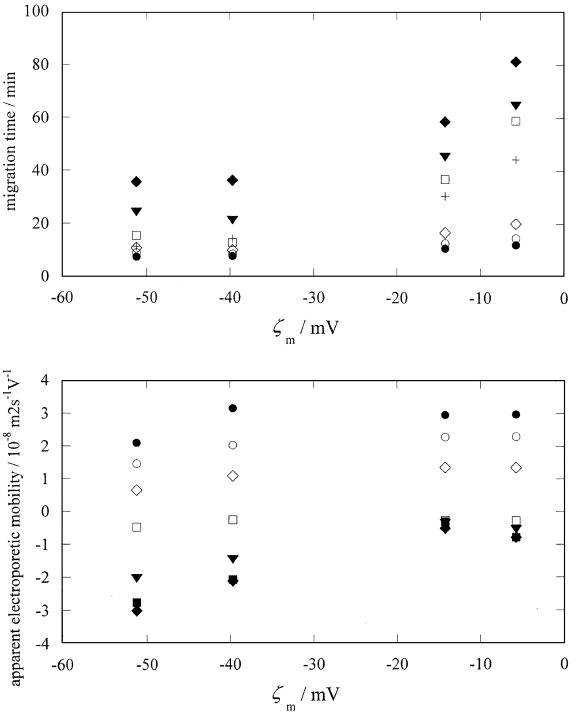

Fig. 4. Effect of ζ_m on the apparent electrophoretic mobility of selected solutes. ζ_m was controlled by varying the type and concentration of salts ($NaClO_4$ and NaCl). Symbols: ●, *N,N*-dimethylbenzylamine; ○, *m*-aminobenzoic acid; ◇, *p*-aminobenzoic acid; □, sulfanilic acid; ▼, *l*-tryptophan; ♦, *o*-nitrophenol; ■, pyrene; +, electroosmotic flow.

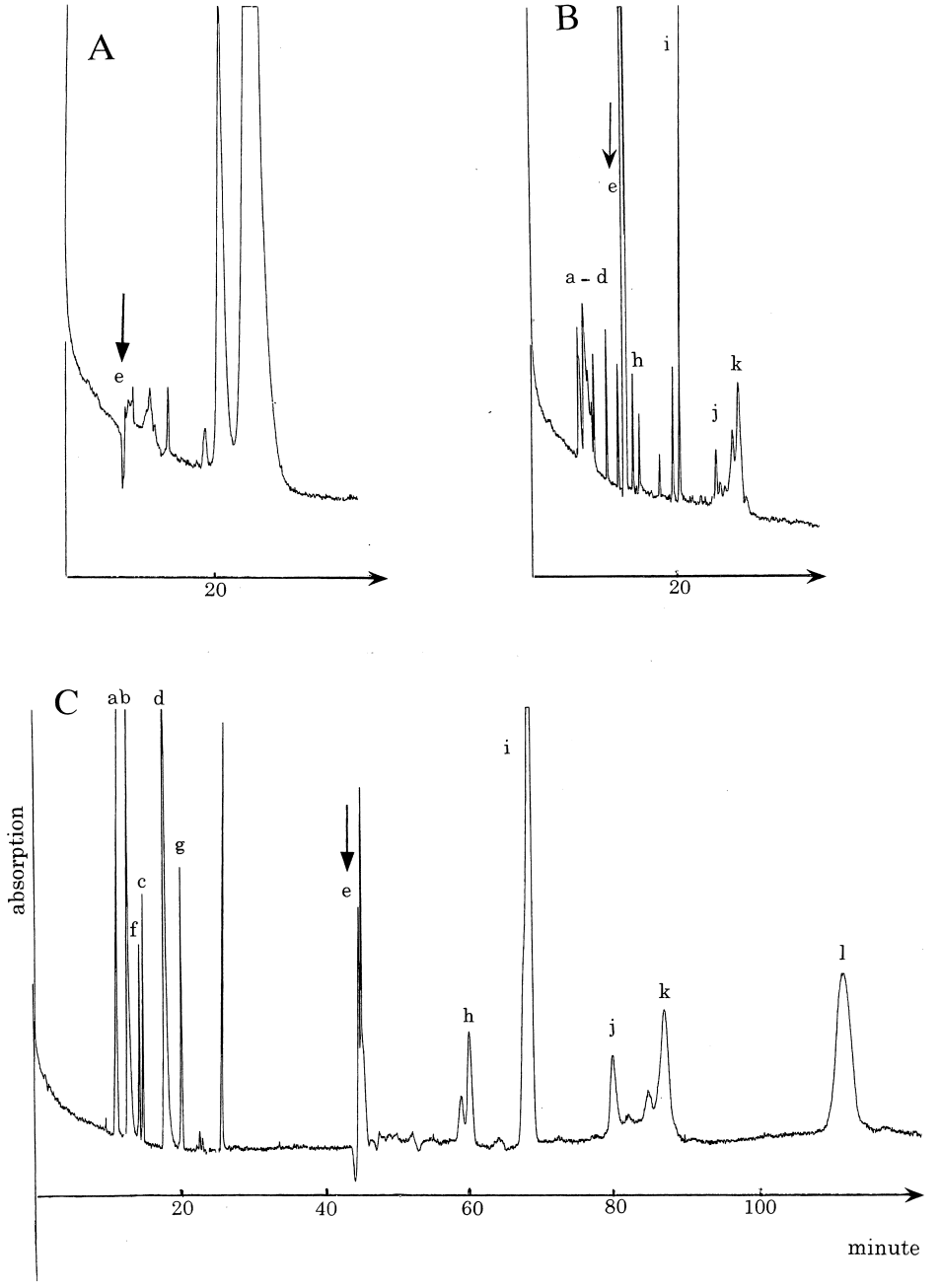

Fig. 5. MEKC separation of selected aromatic compounds. (A) 50 m*M* SDS + 10 m*M* HCl; (B) 50 m*M* DDAPS + 10 m*M* $HClO_4$; (C), 50 m*M* DDAPS + 40 m*M* NaCl + 10 m*M* HCl. Detection at 220 nm. Peaks: (a) phenyltrimethylammonium chloride, (b) 2,4-dimethylpyridine, (c) α-aminoethylbenzene, (d) α-naphthylamine, (e) acetone (electroosmotic flow), (f) *m*-aminobenzoic acid, (g) *p*-aminobenzoic acid, (h) sulfanilic acid, (i) *l*-tryptophan, (j) phenol, (k) *p*-hydroxybenzaldehyde, (l) *o*-nitrophenol.

the nature of an anion still dominantly determines the zeta potential of capillary wall and electroosmotic flow-rates.

3.2.1. Application to the improvements of separation

Since the electrostatic interaction between micelles and solutes is a primary separation mechanism in MEKC, separation of ionic solutes can be modified by varying micellar surface charge densities. For this purpose, anionic/non-ionic mixed micelles have been employed in running buffers, and improved separation of cationic compounds [7]. We believe that the mixed micellar effect should come from reduced charge densities rather than steric hindrance. The zeta potential of sodium dodecylsulfate (SDS) micelle has been reported ca. −100 mV [17], which is higher than that of the DDAPS micelles even in 50 m*M* ClO_4^- solution (ca. −60 mV). Thus, the DDAPS micelles should have natures and/or functions similar to anionic/non-ionic mixed micelles in MEKC separation.

Since, as noted above, the DDAPS micelles have lower charge densities in Cl^- solutions than in ClO_4^- solutions, the zeta potential of the micelles can be successively changed by varying compositions of these electrolytes. Fig. 4 shows the relation between ζ_m and the migration times and apparent electrophoretic mobility of selected solutes. Running solutions were kept acidic (pH 2). Cationic solutes (*N,N*-dimethylbenzylamine, aminobenzoic acids) migrate faster than the electroosmotic flow over the entire ζ_m range examined, meaning that the electrophoresis is more dominant than micellar partition for these compounds. However, their apparent mobility decreases as ζ_m becomes more negative, indicating that these cationic solutes interact with the DDAPS micelles to some extent. Sulfanilic acid and tryptophan should be zwitterionic under this condition, and behave like non-ionic solutes, and migrate at intermediate rates. Thus, the DDAPS carriers are expected to have advantages in separation of cationic solutes because of wider separation windows due to mild electrostatic interactions.

Fig. 5 compares electropherograms obtained with 50 m*M* SDS, 50 m*M* DDAPS + 50 m*M* $NaClO_4$, and 50 m*M* DDAPS + 50 m*M* NaCl. Separation is obviously improved in this order. Cationic compounds are well partitioned to SDS micelles due to strong electrostatic interaction, and not being resolved. The improved resolution in DDAPS micelles is due partly to smaller electroosmotic flow-rate and predominantly to mild micellar electrostatic interaction with cationic compounds.

In conclusion, CE is very effective for the evaluation of small micellar zeta potentials. Such studies allow us (1) to infer the thermodynamic origin in ionic partition into micelles, (2) to discuss the intrinsic nature of the hydration of ions, (3) to control the zeta potential of capillary walls, and (4) to improve CE separation of cationic compounds only by varying electrolytes.

4. Notation

μ	electrophoretic mobility of a solute/m^2 V^{-1} s^{-1}
μ_{eo}	electroosmotic flow mobility/m^2 V^{-1} s^{-1}
V	applied voltage/V
E	applied electric field/V m^{-1}
L	capillary length/m
t_{app}	migration time of a micelle/s
t_{eo}	migration time of EOF/s
ζ_m	zeta potential of a micelle/V
ζ_c	zeta potential of the capillary wall/V
κ	Debye shielding parameter/m^{-1}
a	radius of a spherical micelle/m
η	viscosity of a medium/N s m^{-2}

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