Effect of the polar groups of anionic surfactant on migration behavior in micellar electrokinetic chromatography

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Abstract

Three kinds of anionic surfactants with different polar groups were used as the pseudo-stationary phase in micellar electrokinetic chromatography (MEKC). We found that sodium N-lauroyl-N-methyl-β-alaninate (ALE) can be used as a pseudo-stationary phase in MEKC, as well as sodium N-lauroyl-N-methyltaurate (LMT) and sodium dodecyl sulfate (SDS). The ionic groups are carboxylate, sulfonate and sulfate, respectively. ALE and LMT have amido linkages. The migration behavior of aniline derivatives and phenol derivatives was investigated with these surfactants. The difference in the migration behavior was compared in terms of the capacity factor. Surfactants with amido linkages showed different selectivity from SDS, for phenol derivatives. The three surfactants also gave different selectivity for aniline derivatives. Changing the buffer pH affected greater the migration behavior of aniline derivatives with SDS than those with ALE and LMT. The correlation of the capacity factor and the octanol–water partition coefficient for each solute was also investigated. Correlation with ALE was the highest among the three surfactants. © 1997 Elsevier Science B.V.

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1. Introduction

The migration behavior of solutes is influenced by the nature of the surfactant employed in micellar electrokinetic chromatography (MEKC) [1–3]. Various types of surfactants have been investigated in MEKC. Anionic surfactants with normal alkyl chain and polar group seem to be most widely used, such as sodium dodecyl sulfate (SDS) [1–3], sodium dodecanesulfonate [1], sodium N-lauroyl-N-methyltaurate (LMT) [2,4] and sodium tetradecenesulfonate [2].

We have investigated the effect of the surfactant structure on migration behavior in MEKC. In a previous work [5], we reported the migration behavior with three homologous sodium N-acyl sarcosinates. For hydrophilic solutes, the three sarcosinates give almost the same separation selectivity. Therefore, the structure of the polar moiety in the surfactant is significant in determining the separation selectivity for hydrophilic solutes.

The required properties of surfactants for use as a pseudo-stationary phase in MEKC are: (1) their Krafft points must be lower than ambient temperature and (2) their critical micellar concentrations (CMC values) are not so high as to degrade efficiency.

From a literature search, we found an anionic surfactant, sodium N-lauroyl-N-methyl-β-alaninate (ALE), which could be used as a pseudo-stationary

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phase in MEKC. Although ALE has not been used for MEKC, it satisfies the two requirements [6]. The surfactant has a similar structure to LMT. However, instead of a sulfonate, ALE has a carboxylate as the ionic group. Each of these two surfactants also has an amido linkage. Therefore, we used these surfactants to compare their migration behavior with SDS which is the most commonly used surfactant in MEKC. SDS has a sulfate as the ionic group and no amido linkage.

In this paper, we investigate the suitability of ALE as a pseudo-stationary phase in MEKC. The effect of the polar group of these surfactants on migration behavior in MEKC is also investigated by using aromatic test compounds.

2. Experimental

2.1. Apparatus

MEKC was performed with a CAPI-3000 automated CE System (Otsuka Electronics, Osaka, Japan). A 50 μm I.D. fused-silica capillary (GL Sciences, Tokyo, Japan) of 62 cm total length (50 cm to the detector) was used. The instrument control and data collections were performed with a PC-9801 personal computer (NEC Corporation, Tokyo, Japan).
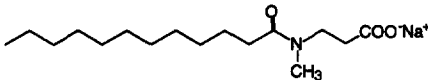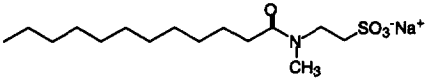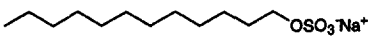
2.2. Reagents

Aromatic test samples, aniline derivatives, cresols, SDS and Sudan IV were obtained from Nacalai Tesque (Kyoto, Japan). Phenol and chlorophenols were obtained from Wako (Osaka, Japan). All reagents were of analytical grade and were used without further purification. ALE was donated by Kawaken (Tokyo, Japan) and LMT by Nikko (Tokyo, Japan). Their purity was checked by elemental analysis. Structures and physicochemical properties of these surfactants in distilled water [6–8] are shown in Table 1.

2.3. Procedure

Running solutions were prepared by dissolving surfactants with concentrations at 50 mM in a mixture of 0.02 M sodium dihydrogenphosphate solution and 0.02 M sodium tetraborate solution adjusted to appropriate pH. Solutions were filtered through a 0.45-μm membrane filter prior to use.

Stock solutions of aromatic test samples were prepared in 20% (v/v) methanol in water. Sample solutions for injection were made by tenfold diluting

Table 1
Structures and physicochemical properties of surfactants in distilled water [6–8]

Surfactant	Krafft point / °C	CMC / mM
Sodium N-lauroyl-N-methyl-β-alaninate (ALE)	<20	9.8 (40 °C)
Sodium N-lauroyl-N-methyltaurate (LMT)	<0	8.7 (35 °C)
Sodium dodecyl sulfate (SDS)	16	8.6 (40 °C)

the stock solution with running buffer. Each concentration of solute was about 100 mg/l.

When the running solution was changed, the capillary was rinsed with 0.1 M NaOH for 5 min using a vacuum at the detector reservoir, and then purged with distilled water for 3 min and running buffer for 4 min. After each run, the capillary was rinsed with running buffer for 4 min.

Sample injections were made hydrostatically, 20 mm×30 s. The injection volume was about 1.7 nl. The set-up voltage and temperature were 20 kV and 30°C, respectively, throughout all experiments. Migrated samples were detected by on-column measurement of UV absorption with photo-diode array detector at the range of 200 to 400 nm.

3. Results and discussion

3.1. The dependence of the migration behavior on surfactants

The migration behavior of phenol derivatives and aniline derivatives with three surfactants was investigated using 50 mM of each surfactant in the buffer with a pH of 7.0. ALE was easily dissolved in the buffer at ambient temperature and was able to be used as a pseudo-stationary phase in MEKC.

Physicochemical properties of aromatic test samples [9–11] are shown in Table 2. Phenol derivatives are acidic substances whereas aniline derivatives are basic substances. Three times measurements were made for all runs and the average values were used in the paper. Relative standard deviations of the migration time and the capacity factor of solutes were within 1.7 and 1.0%, respectively. The chromatograms are shown in Fig. 1 and Fig. 2.

In MEKC [1], the capacity factor of an electrically neutral solute is given by:
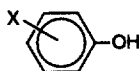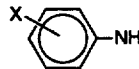
$$k' = \frac{t_R - t_0}{t_R(1 - t_0/t_{mc})} \quad (1)$$

where t_R, t_0 and t_{mc} are the migration time for the solute, methanol (used as a tracer for the electroosmotic flow) and Sudan IV (used as a tracer for the micelle).

Fig. 3 shows the dependence of the capacity

Table 2
Structures and physicochemical properties of aromatic test samples [9–11]

Test samples	X	log P_{ow}	pK_a
Phenol derivatives	1. None	1.49	9.89
	2. o-Me	No data	10.20
	3. m-Me	1.96	10.01
	4. p-Me	1.94	10.17
	5. o-Cl	2.17	8.49
	6. m-Cl	2.49	8.85
	7. p-Cl	2.45	9.18
Aniline derivatives	1. None	0.90	4.63
	2. o-Me	1.35	4.44
	3. m-Me	1.41	4.73
	4. p-Me	1.40	5.08
	5. o-Cl	1.91	2.65
	6. m-Cl	1.99	3.46
	7. p-Cl	1.83	4.15

factors of phenol derivatives on the surfactants. The capacity factors with ALE and LMT are almost the same in spite of the difference of their ionic group. The capacity factors with SDS are smaller than those with ALE and LMT. They showed similar separation selectivity for phenol derivatives. The migration behavior of phenol derivatives was affected by the existence of amido linkage.

The dependence for aniline derivatives is shown in Fig. 4. The capacity factors with ALE were slightly smaller than those with LMT, but the separation selectivity with ALE was almost the same as that with LMT. It should be noted that the capacity factors with SDS were in contrast to those with another surfactant. p-Toluidine and m-toluidine have higher pK_a values than the other aniline derivatives and strongly interact with SDS micelles. Therefore, the separation with SDS seemed to be controlled by electrostatic interaction.

3.2. The dependence of the migration behavior on pH

To investigate the effect of pH on migration behavior of aniline derivatives, other buffer solutions, pH 8.0 and 9.0 were used. Figs. 5–7 show the pH dependence of migration behavior with three surfactants. The capacity factors of all solutes with ALE and LMT slightly varied with pH, however, the
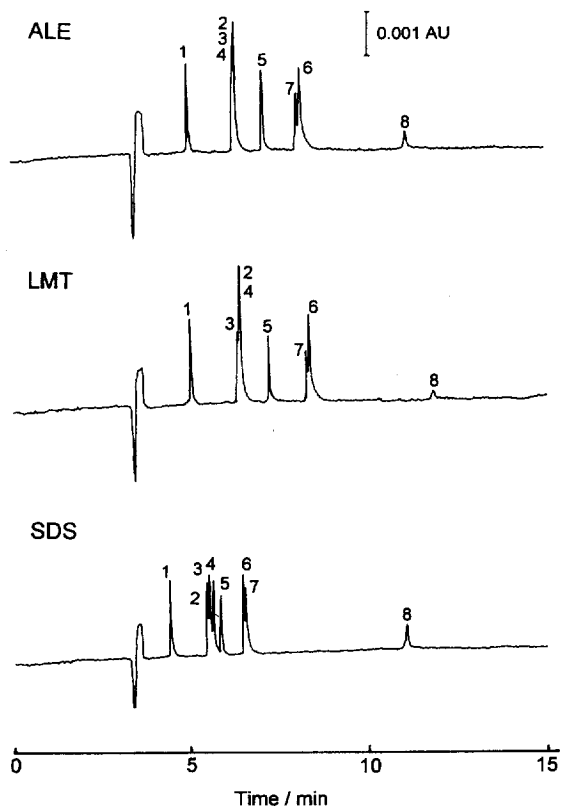
Fig. 1. Chromatograms of phenol derivatives with three surfactants. Conditions: Capillary, 62 cm (50 cm to the detector)×50 mm I.D.; concentration of surfactants, 50 mM; running buffer, 0.02 M borate-phosphate (pH 7.0); applied voltage, 20 kV; detection wavelength, 270 nm; temperature, 30°C. Peak identification: 8 = Sudan IV; for the other peaks see Table 1.
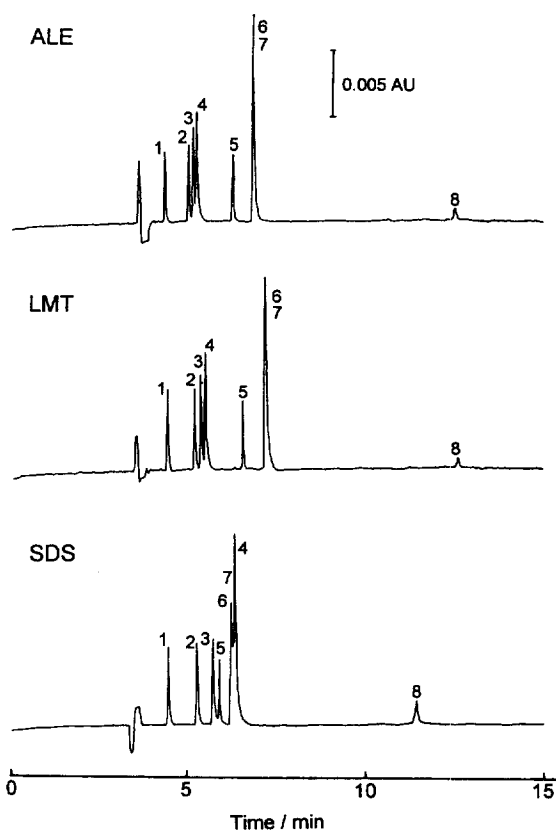

Fig. 2. Chromatograms of aniline derivatives with three surfactants. Conditions: detection wavelength, 240 nm. Other conditions as in Fig. 1. Peak identification: 8 = Sudan IV; for the other peaks see Table 1.

capacity factors of p-toluidine and m-toluidine with SDS showed large variations with pH. A similar dependence was also observed for p-anisidine and N-methylaniline in our previous work [12]. The pK_a values of these derivatives are relatively higher than those of the other derivatives. Therefore, we consider that the dependence is caused by the slight ionization of the solute.

3.3. The correlation of the capacity factors and octanol–water partition coefficients

It is widely known that hydrophobic interactions are the main driving force controlling the separation in MEKC [3]. The logarithm of octanol–water partition coefficient ($\log P_{ow}$) is generally used for
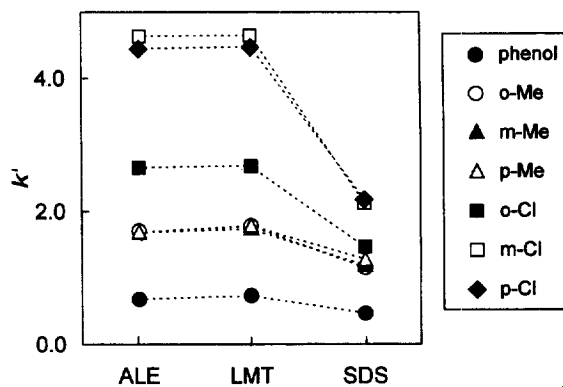

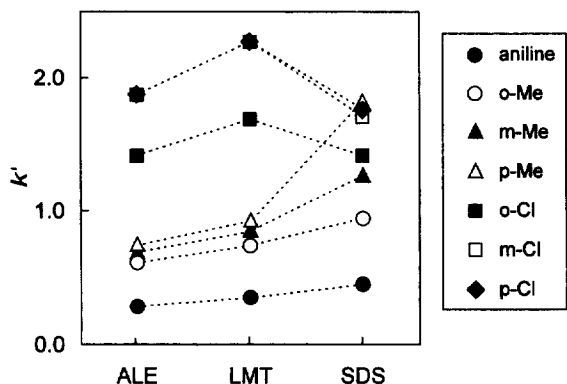Fig. 3. Dependence of the capacity factor of phenol derivatives on surfactants (pH 7).

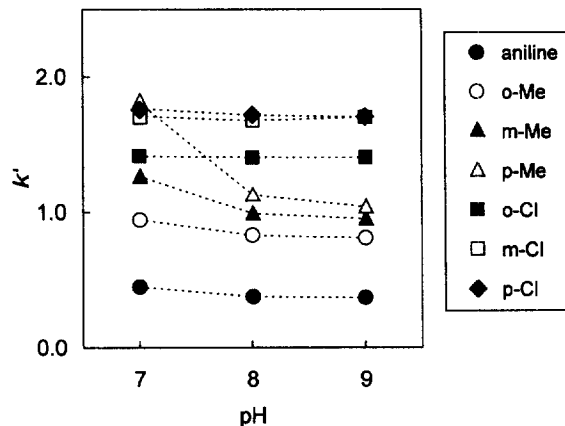Fig. 4. Dependence of the capacity factor of aniline derivatives on surfactants (pH 7).
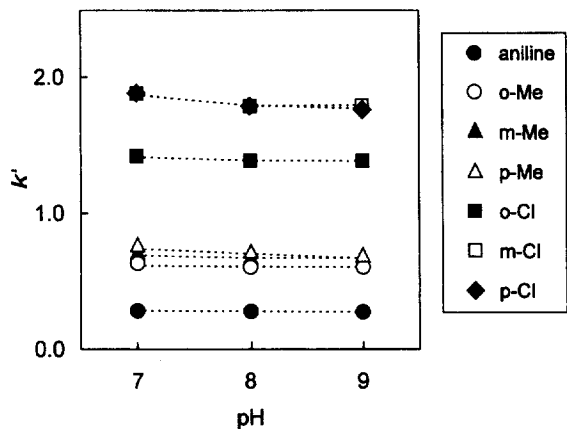

Fig. 5. Dependence of the capacity factor of aniline derivatives with ALE on pH.

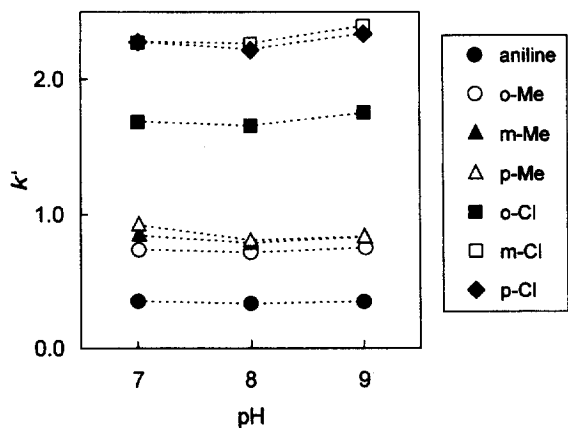Fig. 6. Dependence of the capacity factor of aniline derivatives with LMT on pH.

Fig. 7. Dependence of the capacity factor of aniline derivatives with SDS on pH.

the measure of hydrophobicity. Several papers mentioned the linear relationship between the migration behavior in MEKC and $\log P_{ow}$ of solutes. Smith et al. applied MEKC with SDS for the rapid screening method of $\log P_{ow}$ values [13].

Therefore, to investigate the relationship between the migration behavior and the hydrophobicity of these solutes with three different surfactants, the logarithms of capacity factor of solutes at pH 7 were plotted against $\log P_{ow}$ values. These results are shown in Fig. 8. For ALE and LMT, linear relationships with high correlation coefficients were observed. The correlation with SDS was lower than those with ALE and LMT. As the capacity factors with SDS, p-toluidine and m-toluidine deviated from
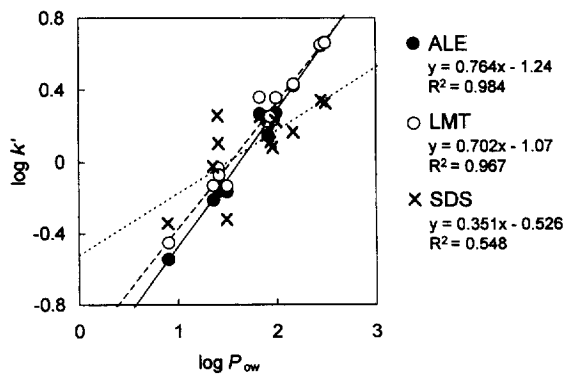

Fig. 8. Correlations of the logarithm of capacity factor vs. $\log P_{ow}$ of each derivative with three surfactants.

the fitting curve. These results suggest that the electrostatic interaction of solutes and micelles in ALE and LMT is not as strong as that in SDS. This suggests that the existence of amido linkage in the structure of surfactant suppresses the electrostatic interaction between the surfactants and solutes.

4. Conclusion

ALE was used as a pseudo-stationary phase in MEKC. The migration behavior with ALE was compared to that with LMT and SDS. For the phenol derivatives and aniline derivatives we used, the presence of amido linkage affected greater their migration behavior than the difference of ionic group. The result can be explained by the different contribution of electrostatic interaction among the surfactants. The logarithms of capacity factor with ALE gave the best correlation among the three surfactants. ALE can be used for the estimation of $\log P_{ow}$ by MEKC. It is necessary to extend the measurement of other various substances.

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