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Short communication

Separation of naphthalene and flavone derivatives by micellar electrokinetic chromatography with double- and triple-chain surfactants

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Abstract

Three surfactants, *p*-bis(2-dodecyloxymethyl-3-oxa-6-sodiosulfonatohexyloxy)benzene (BDSB) having two sulfonate groups and two lipophilic chains, disodium 10-dodecanoyl-5,15-bis(dodecyloxymethyl)-10-aza-4,7,13,16-tetraoxa-1,19-nonadecanedisulfonate (DDBTN) having two sulfonate groups and three lipophilic chains and disodium 4,11-bis(dodecyloxymethyl)-3,6,9,12-tetraoxa-1,14-tetradecanedionate (DBTT) having two carboxylate groups and two lipophilic chains, were used in micellar electrokinetic chromatography (MEKC). Eight naphthalene derivatives were baseline separated at 10 m*M* BDSB or 5 m*M* DBTT, and five flavone derivatives at 5 m*M* BDSB, DDBTN or DBTT. The elution order of the naphthalene derivatives in MEKC with BDSB was identical with that with DDBTN. However, this elution order was different from that found with DBTT. In the case of the flavone derivatives, BDSB, DDBTN and DBTT produced the identical elution order. These double- and triple-chain surfactants exhibited different selectivity when compared with widely used sodium dodecyl sulfate.

Keywords: Flavones; Naphthalene derivatives; Surfactants, multi-chain

1. Introduction

Micellar electrokinetic chromatography (MEKC) is a variation of capillary electrophoresis and has been developed for the separation of non-ionic compounds. Recently, MEKC has been applied to separating a variety of analytes such as bases, nucleosides and oligonucleotides [1], medicines [2], environmental pollutants [3], enantiomers [4], etc. In previous papers [5,6], we introduced three double-chain surfactants with a different connecting linkage between the two lipophilic chains in MEKC, i.e. disodium 5,12-bis(dodecyloxymethyl)-4,7,10,13-tetraoxa-1,16-hexadecanedisulfonate, 5,13-bis(dodecyloxymethyl)-4,7,11,14-tetraoxa-1,17-heptadecanedisulfonate and 5,13-bis(dodecyloxymethyl)-4,7,11,14-tetraoxa-9,9-dimethyl-1,17-heptadecanedisulfonate, which were derived from ethylene glycol diglycidyl ether, 1,3-propanediol diglycidyl ether and 2,2-dimethyl-1,3-propanediol diglycidyl ether, respectively. These surfactants with two sulfonate

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groups, exhibited a remarkably different MEKC selectivity, wider migration time windows and the separation performance at concentrations at least one order of magnitude lower, in comparison with sodium dodecyl sulfate (SDS), a widely used surfactant with one sulfate group and one lipophilic chain.

In this paper, preliminary results are described on the MEKC behaviours of a double-chain and a triple-chain surfactants with two sulfonate groups derived from hydroquinone diglycidyl ether and N-dodecanoyldiethanolamine diglycidyl ether, respectively, and a double-chain surfactant with two carboxylate groups derived from ethylene glycol diglycidyl ether. These multi-chain surfactants are briefly compared with SDS, as micelle-forming reagents in the MEKC separations of several naphthalene and flavone derivatives.

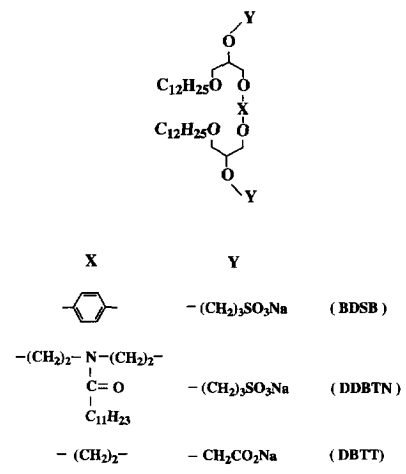

Fig. 1. Structures of surfactants.

2. Experimental

2.1. Apparatus

MEKC was carried out using an Applied Biosystems Model 270A capillary electrophoresis system (California, USA) with a fused-silica capillary tube (72 cm×50 μm I.D., 50 cm from inlet to detector). The separation temperature was held constant at 30°C and the applied voltage at 15 kV for naphthalene derivatives or at 20 kV for flavone derivatives. The naphthalene and flavone derivatives were detected by UV absorption at 210 and 280 nm, respectively. A Hitachi D-2500 Chromato-Integrator (Hitachi, Japan) was used for data processing. All experiments were performed in duplicate to ensure reproducibility.

2.2. Reagents

The structures of the double- and triple-chain surfactants used in this work are shown in Fig. 1. *p*-Bis(2-dodecyloxymethyl-3-oxa-6-sodiosulfonatohexyloxy)benzene (BDSB) and disodium 10-dodecanoyl - 5,15 - bis(dodecyloxymethyl) - 10 - aza - 4,7, 13,16-tetraoxa-1,19-nonadecanedisulfonate (DDBTN) were synthesized according to modified procedures using hydroquinone diglycidyl ether [7] and N-dodecanoyldiethanolamine diglycidyl ether [8], respectively. Disodium 4,11-bis(dodecyloxymethyl)-3,6,9,12-tetraoxa-1,14-tetradecanedionate (DBTT) was prepared by reaction of 1,8-bis(dodecyloxymethyl)-3,6-dioxa-1,8-octanediol with bromoacetic acid [9]. All other reagents were of analytical-reagent grade and were used as received.

Separation solutions were prepared by dissolving the surfactants in a buffer solution of 0.05 *M* sodium dihydrogenphosphate–0.1 *M* sodium borate at pH 7.0 for the naphthalene derivatives and at pH 9.0 for the flavone derivatives. Methanol was used as a marker of the electro-osmotic flow and Sudan III as the micelle tracer.

3. Results and discussion

3.1. Separations of naphthalene and flavone derivatives

The separations of eight monosubstituted naphthalene derivatives used were performed in the surfactant concentration range of 1.0–10.0 m*M* in the separation buffer at pH 7.0. The naphthalene derivatives were baseline separated at 10.0 m*M* BDSB (Fig. 2a) and at above 5.0 m*M* DBTT (Fig. 2c), respectively. On the other hand, the separation of 1-naphthol and 1-nitronaphthalene could not be

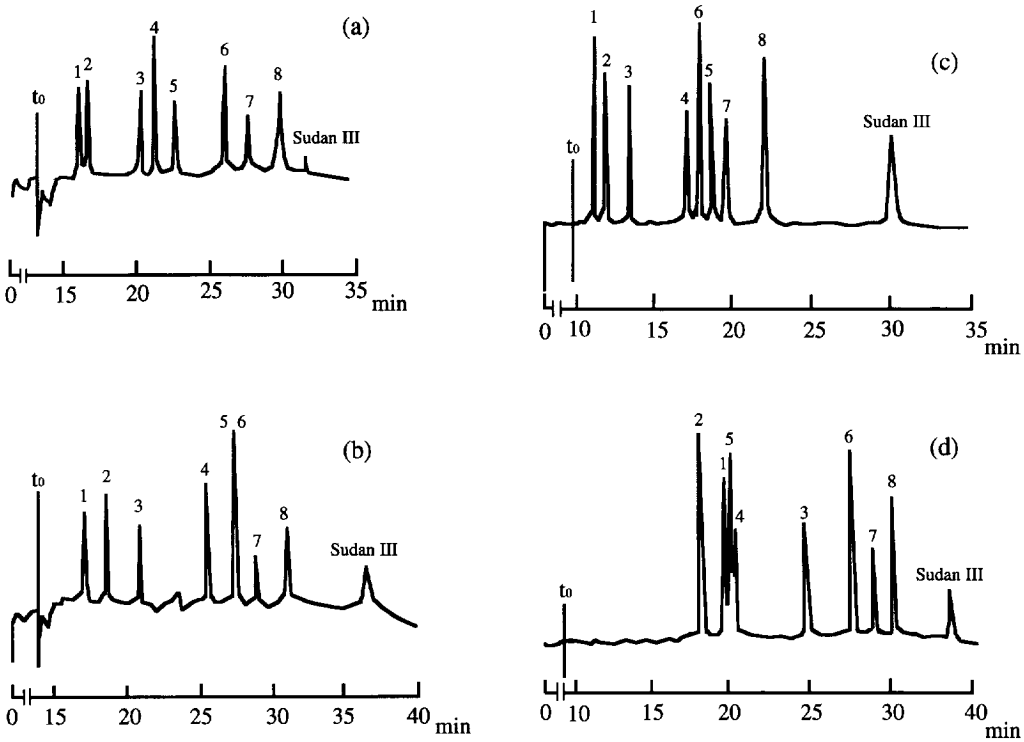

Fig. 2. Separations of naphthalene derivatives with (a) 10.0 m*M* BDSB, (b) 10.0 m*M* DDBTN, (c) 5.0 m*M* DBTT and (d) 25.0 m*M* SDS. Peaks: 1=1-naphthalenemethanol, 2=1-naphthylamine, 3=1-naphthaleneethanol, 4=2-naphthol, 5=1-naphthol, 6=1-nitronaphthalene, 7=2-methoxynaphthalene, 8=1-methoxynaphthalene.

attained even at a concentration of 10.0 m*M* in the DDBTN system (Fig. 2b).

The separation of five flavone derivatives was also attempted by MEKC with these surfactants (3.0–10.0 m*M*). Typical chromatograms for the separation of the analytes are shown in Fig. 3. The flavone derivatives could be baseline separated with these surfactants at concentrations above 5.0 m*M* at pH 9.0 (Fig. 3a–c), though not at all at pH 7.0 (not shown). On the other hand, 6-hydroxyflavone and 3-hydroxyflavone could not be resolved even at 10.0–50.0 m*M* SDS at pH 9.0.

3.2. Comparison of surfactants

The capacity factors (k') of the naphthalene derivatives were calculated (Table 1) and plotted against the concentration of BDSB, DDBTN, DBTT or SDS. From the results of the regression analyses in these surfactant systems, good linear relationships were obtained for each analyte. This suggests that the distribution coefficients of each analyte remain constant at least in the measured concentration range.

The elution order of the naphthalene derivatives in MEKC with double-chain BDSB (Fig. 2a) and triple-chain DDBTN (Fig. 2b) having two sulfonate groups is identical, though the elution time of each analyte in MEKC with DDBTN is longer. The elution order with these surfactants is the same as that with the previously reported double-chain surfactants with two sulfonate groups [6], which differ in the structure of the linkage between the two dodecyl chains. The elution order in MEKC with DBTT having two carboxylate groups, was different from that found with the above-mentioned surfactants having sulfonate groups, i.e. the elution order of 1-nitronaphthalene and 1-naphthol was reversed (Fig. 2c). These multi-chain surfactants exhibited remarkably different selectivities, compared with the elution order in the single-chain SDS system (Fig. 2d). The HPLC

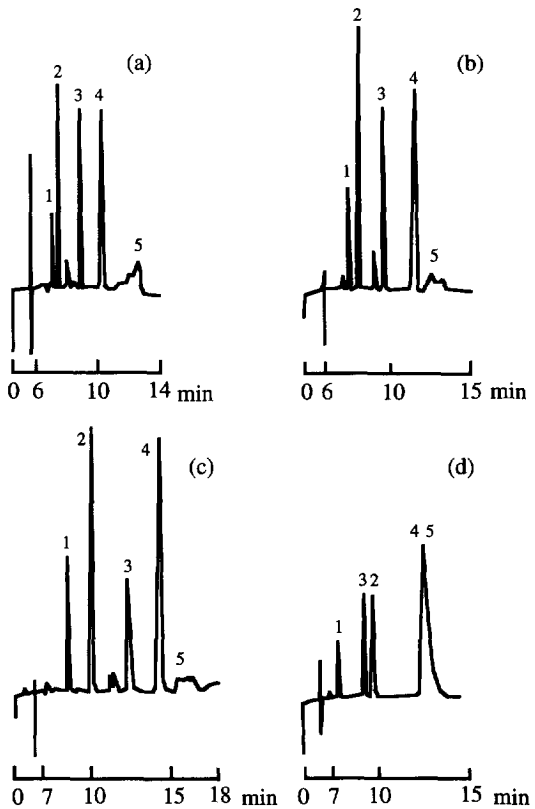

Fig. 3. Separations of flavone derivatives with (a) 5.0 m*M* BDSB, (b) 5.0 m*M* DDBTN, (c) 5.0 m*M* DBTT and (d) 25.0 m*M* SDS. Peaks: 1=3′,5,7-trihydroxy-4′-methoxyflavone, 2=7-hydroxyflavone, 3=4′,5,7-trihydroxyflavone, 4=6-hydroxyflavone, 5=3-hydroxyflavone.

elution order of the analytes on an ODS column eluted with water–acetonitrile (45:55) is 1-naphthalenemethanol < 1-naphthaleneethanol < 2-naphthol < 1-naphthylamine < 1-naphthol < 1-nitronaphthalene < 2-methoxynaphthalene < 1-methoxynaphthalene. This order is identical with that in the MEKC systems of the multi-chain surfactants having two sulfonate groups, except that 1-naphthylamine eluted between 2- and 1-naphthol.

Table 1
Capacity factors of naphthalene derivatives in MEKC with 10.0 m*M* BDSB, DDBTN, DBTT and SDS

Analyte	BDSB	DDBTN	DBTT	SDS
1-Naphthalenemethanol	0.43	0.42	2.01	0.88
1-Naphthylamine	0.53	0.67	2.50	0.68
1-Naphthaleneethanol	1.45	1.15	3.50	1.84
2-Naphthol	1.84	2.73	7.36	0.97
1-Naphthol	2.54	3.84	9.86	0.94
1-Nitronaphthalene	5.49	3.84	8.70	2.71
2-Methoxynaphthalene	8.44	5.01	11.6	3.32
1-Methoxynaphthalene	21.7	8.06	18.5	4.08

As shown in Fig. 3a–c, BDSB, DDBTN and DBTT gave an identical MEKC elution order for the flavone derivatives. This elution order was clearly different from that with SDS (Fig. 3d). The elution order of 7-hydroxyflavone and 4′,5,7-trihydroxyflavone was reversed and 6- and 3-hydroxyflavone were co-eluted in the SDS system. The elution order of 4′,5,7-trihydroxyflavone<3′,5,7-trihydroxy-4′-methoxyflavone = 7-hydroxyflavone < 6-hydroxyflavone<3-hydroxyflavone was observed in HPLC on an ODS column eluted with water–acetonitrile (50:50). Thus, these three separation systems gave the different elution orders for the flavone derivatives. The results suggest that the analytes bearing a hydroxyl group at their 7-positions interact less with the micelles and ODS. The peak shape of 3-hydroxyflavone (Fig. 3a–c) was not normal. The reason for this is not clear now but may relate to a broad tailing HPLC peak of 3-hydroxyflavone on the ODS column.

Thus, the multi-chain surfactants show remarkably different selectivity of the naphthalene and flavone derivatives, compared with single-chain SDS. The MEKC elution order of the analytes with these surfactants including SDS is not necessarily related to the hydrophobicity of the analytes, compared with the elution order in HPLC. Therefore, other effects such as hydrogen bonding must be considered in order to convincingly explain the change in the MEKC elution order. The baseline separations of both derivatives could be performed with the multi-chain surfactants at lower concentrations than with SDS. The application of these multi-chain surfactants to real samples is of great interest.

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References

[1] A.S. Cohen, S. Terabe, J.A. Smith and B.L. Karger, Anal. Chem., 59 (1987) 1021–1027.
[2] H. Nishi, N. Tsumagari and S. Terabe, Anal. Chem., 61 (1989) 2434–2439.
[3] C.L. Copper and M.J. Sepaniak, Anal. Chem., 66 (1994) 147–154.
[4] S. Terabe, M. Shibata and Y. Miyashita, J. Chromatogr., 480 (1989) 403–411.
[5] M. Tanaka, T. Ishida, T. Araki, A. Masuyama, Y. Nakatsuji, M. Okahara and S. Terabe, J. Chromatogr., 648 (1993) 469–473.
[6] H. Harino, M. Tanaka, T. Araki, Y. Yasaka, A. Masuyama, Y. Nakatsuji, I. Ikeda, K. Funazo and S. Terabe, J. Chromatogr. A, 715 (1995) 135–141.
[7] Y.-P. Zhu, A. Masuyama, T. Nagata and M. Okahara, J. Jpn. Oil. Chem. Soc. (Yukagaku), 40 (1991) 473–477.
[8] Y.-P. Zhu, A. Masuyama, Y. Kirito and M. Okahara, J. Am. Oil. Chem. Soc., 68 (1991) 539–543.
[9] Y.-P. Zhu, A. Masuyama, Y. Kobata, Y. Nakatsuji, M. Okahara and M.J. Rosen, J. Colloid Interface Sci., 158 (1993) 40–45.