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Double-chain surfactants with two sulfonate groups as micelle-forming reagents in micellar electrokinetic chromatography of naphthalene derivatives

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Abstract

Three surfactants having two sulfonate groups and two lipophilic chains, disodium 5,12-bis(dodecyloxymethyl)-4,7,10,13-tetraoxa-1-16-hexadecanedisulfonate (DBTHX), 5,13-bis(dodecyloxymethyl)-4,7,11,14-tetraoxa-1-17-heptadecanedisulfonate (DBTHP) and 5,13-bis(dodecyloxymethyl)-4,7,11,14-tetraoxa-9,9-dimethyl-1-17-heptadecanedisulfonate (DBTDMHP), were used in micellar electrokinetic chromatography (MEKC) to separate eight naphthalene derivatives as model analytes. Their capacity factors linearly increased as the concentration of each surfactant increased from 1 to 10 m*M* at pH 7.0. These double-chain surfactants exhibited different selectivity and wider migration time windows when compared with sodium dodecyl sulfate (SDS), which is used widely in MEKC. The eight naphthalene derivatives were baseline separated at 5 m*M* DBTHX and 2.5 m*M* DBTHP, respectively, and nearly baseline separated at 2.5 m*M* DBTDMHP. However, SDS at 60 m*M* could not completely resolve three of the analytes.

1. Introduction

Micellar electrokinetic chromatography (MEKC) [1] has been developed for the separation of electrically neutral analytes by electrophoresis with an ionic micellar solution as the separation solution, and has attracted much attention in various fields. Since the MEKC separation principle is based on differential partitioning of the analyte between the micelle and the surrounding aqueous phase, the choice of surfactant significantly affects MEKC selectivity. Therefore, the introduction of new types of surfactants for MEKC is of great interest and is expected to be useful in modulating its selectivity.

Recently, one of the authors has shown that amphipathic compounds with two sulfate or sulfonate groups and two long alkyl chains, which are derived from glycol diglycidyl ethers,

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have good water solubility and excellent surface active properties in water [2,3]. In particular, disodium 5,12-bis(dodecyloxymethyl)-4,7,10,13-tetraoxa-1-16-hexadecanedisulfonate (DBTHX) had a very low critical micelle concentration (CMC) (0.014 m*M*) and a low Krafft point (below 0°C). In a previous paper [4], we applied this double-chain surfactant in MEKC for the first time and compared it with sodium dodecyl sulfate (SDS), a widely used surfactant with one ionic group and one lipophilic chain. For several benzene and naphthalene derivatives, DBTHX exhibited promising results (i.e., different selectivity and a wider migration time window).

In the present paper, we describe the synthesis of new double-chain surfactants such as disodium 5,13-bis(dodecyloxymethyl)-4,7,11,14-tetraoxa-1,17-heptadecanedisulfonate (DBTHP) and 5,13-bis(dodecyloxymethyl)-4,7,11,14-tetraoxa-9,9-dimethyl-1,17-heptadecanedisulfonate (DBTDMHP), which differ from DBTHX in the structure of the linkage between the two lipophilic chains. These three double-chain surfactants are compared with SDS, a typical single-chain surfactant, as micelle-forming reagents in the MEKC of naphthalene derivatives.

2. Experimental

2.1. Apparatus

MEKC was carried out using an Applied Biosystems Model 270A capillary electrophoresis system (CA, USA) with a fused-silica capillary tube (72 cm × 50 μm I.D., 50 cm from inlet to detector). The temperature and applied voltage for separation were held constant at 30°C and 15 kV, respectively. UV detection was at 210 nm. A Hitachi D-2500 Chromato-Integrator (Hitachi, Japan) was used for data processing.

Sample solutions ($1.0 \cdot 10^{-2}$% in 10% methanol) were injected using a vacuum technique (12.7 cmHg pressure difference for 0.5 s). All experiments were performed in duplicate to ensure reproducibility.

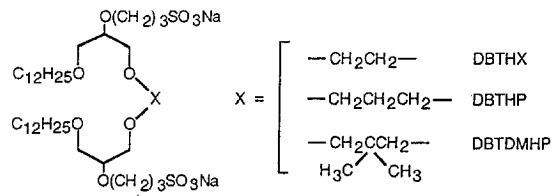

Fig. 1. Structures of double-chain surfactants.

2.2. Reagents

The structures of the double-chain surfactants are shown in Fig. 1. DBTHP and DBTDMHP were synthesized using 1,3-propanediol diglycidyl ether and 2,2-dimethyl-1,3-propanediol diglycidyl ether, respectively, instead of ethylene glycol diglycidyl ether for DBTHX as previously reported [2]. 1,3-Propanediol diglycidyl ether and 2,2-dimethyl-1,3-propanediol diglycidyl ether were obtained by the reaction of epichlorohydrin with 1,3-propanediol and 2,2-dimethyl-1,3-propanediol, respectively. The isolated double-chain surfactants were identified by MS and NMR spectra and elemental analysis. The purity of the surfactants was more than 99%. Several physico-chemical properties of the surfactants are given in Table 1, together with their yields based on the corresponding diols treated with propanesulfone. All other reagents were of analytical-reagent grade and used as received.

Separation solutions were prepared by dissolving the double-chain surfactants in a buffer solution of 0.1 *M* sodium dihydrogenphosphate–

Table 1
Several physico-chemical properties of double-chain surfactants

	Surfactant		
	DBTHX	DBTHP	DBTDMHP
Molecular mass	823.111	837.146	865.200
CMC (m*M*)	0.014	0.017	0.0043
Krafft point (°C)	<0	<0	<0
Yield[a] (%)	68	83	48

[a] Based on diols.

0.05 *M* sodium borate at pH 7.0. Methanol was used as a marker of the electroosmotic flow and Sudan III was used as the micelle tracer.

3. Results and discussion

3.1. Separation of model analytes

The structures of the eight monosubstituted naphthalene derivatives used as analytes in this study are shown in Fig. 2. Their migration times were measured at five double-chain surfactant concentrations between 1.0 and 10.0 m*M* in 0.1 *M* phosphate–0.05 *M* borate buffer at pH 7.0. All the analytes were baseline separated with DBTHX and DBTHP at concentrations above 5.0 and 2.5 m*M*, respectively, and almost baseline separated with DBTDMHP above 2.5 m*M*. In the DBTDMHP system, the complete baseline separation of 1-naphthalenemethanol and 1-naphthylamine could not be attained even at 10.0 m*M* DBTDMHP. Typical chromatograms for the separation of the analytes using these double-chain surfactants are shown in Fig. 3.

MEKC with SDS was also performed in a concentration range of 10–60 m*M*. In this case, 1-naphthalenemethanol, 1-naphthol and 2-naphthol could not be baseline separated even at 60 m*M* SDS (chromatogram not shown).

3.2. Comparison of surfactants

The capacity factor of a neutral analyte in MEKC can be calculated using the following equation [1].

$$k' = \frac{t_R - t_o}{t_o(1 - t_R/t_{mc})} \quad (1)$$

where t_R, t_o and t_{mc} are the migration times of the analyte, the solute which does not interact with the micelle (methanol peak) and the micelle (Sudan III peak), respectively. When the micellar concentrations are low, k' is approximately related to the surfactant concentration using Eq. 2 [5].

$$k' = Kv(C_{sf} - CMC) \quad (2)$$

where K is the distribution coefficient of the analyte, and v and C_{sf} are the partial specific volume of the micelle and the surfactant concentration, respectively.

The plots of calculated k' for the eight naphthalene derivatives vs. concentration of each surfactant are shown in Fig. 4. The capacity

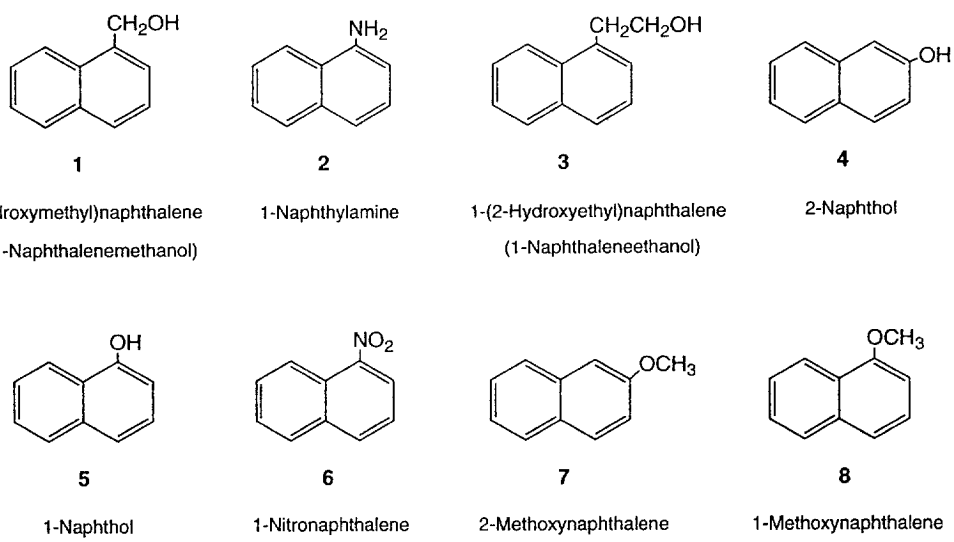

Fig. 2. Structures of naphthalene derivatives used as model analytes.

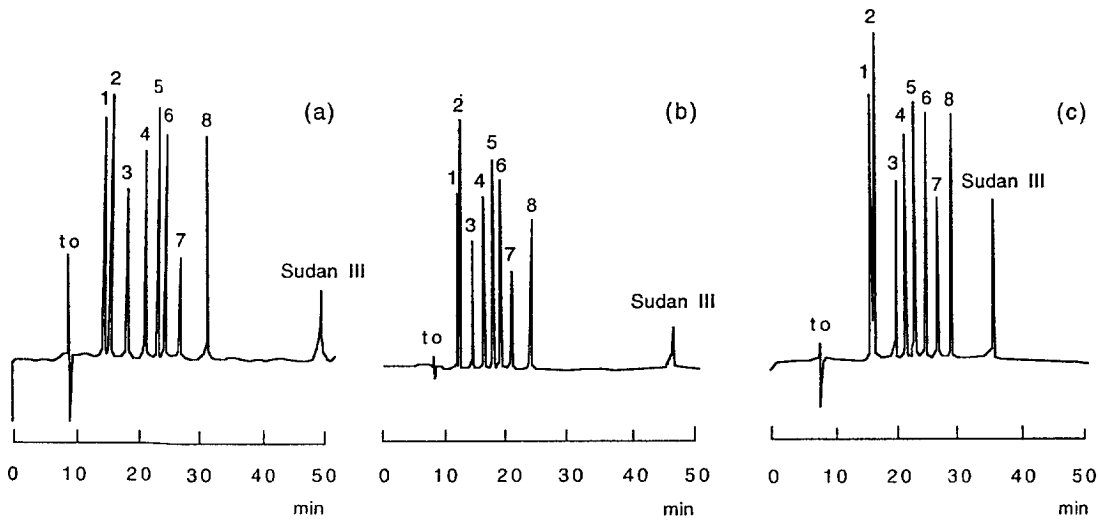

Fig. 3. Separations of naphthalene derivatives with (a) 5.0 m*M* DBTHX, (b) 2.5 m*M* DBTHP and (c) 2.5 m*M* DBTDMHP. Peak numbers same as in Fig. 2.

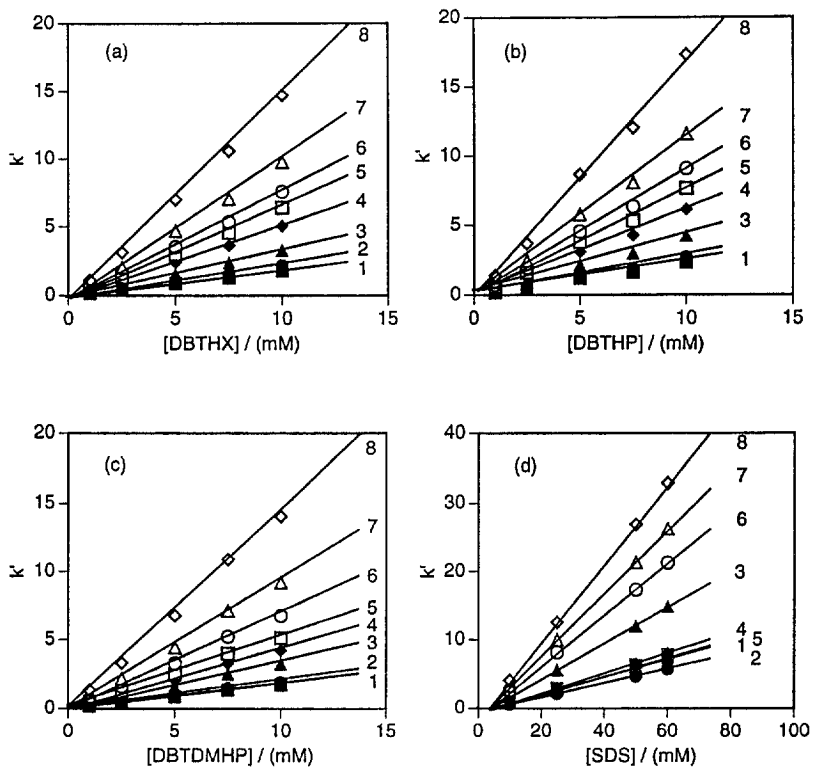

Fig. 4. Dependence of calculated capacity factor (k') of naphthalene derivatives on concentration of (a) DBTHX, (b) DBTHP, (c) DBTDMHP and (d) SDS. Analyte numbers same as in Fig. 2.

factors of the analytes increased linearly with an increase in the concentration of each surfactant (1.0–10 m*M* for DBTHX, DBTHP or DBTDMHP and 10–60 m*M* for SDS). For DBTHX, DBTHP and DBTDMHP, the current only increased from 26 to 28 μA with an increase of the surfactant concentration from 1.0 to 10 m*M*. For SDS, on the other hand, a current increase from 25 (10 m*M*) to 33 μA (60 m*M*) was observed. Table 2 gives the results of the regression analyses for the double-chain surfactants. Good linear relationships (correlation coefficient range: more than 0.993) were obtained for each analyte, which suggests that the distribution coefficients remain constant at least in the measured concentration range. Similar linear plots were also obtained for SDS.

From Eq. 2, the intercepts of the plots in Fig. 4 extrapolated to $k' = 0$ can be interpreted to be the CMC of the surfactant under the MEKC conditions used. The averaged CMC values estimated for DBTHX, DBTHP and DBTDMHP are 0.283, 0.325 and 0.058 m*M*, respectively. Their CMC values in pure water were also determined from the break points of the surface tension (measured with a Wilhelmy tensiometer at 20°C) vs. concentration plots. The resulting CMC values are 0.014, 0.017 and 0.0043 m*M* for DBTHX, DBTHP and DBTDMHP, respectively (Table 1). The CMC

Table 2
Correlation between concentration of surfactant and capacity factor

Analyte	Surfactant	Regression equation	Correlation coefficient
1-Naphthalenemethanol	DBTHX	$y = 0.182x - 0.037$	0.999
	DBTHP	$y = 0.240x - 0.093$	0.993
	DBTDMHP	$y = 0.177x + 0.003$	0.998
1-Naphthylamine	DBTHX	$y = 0.223x - 0.063$	0.998
	DBTHP	$y = 0.281x - 0.116$	0.994
	DBTDMHP	$y = 0.194x - 0.015$	0.998
1-Naphthaleneethanol	DBTHX	$y = 0.337x - 0.007$	0.999
	DBTHP	$y = 0.436x - 0.129$	0.994
	DBTDMHP	$y = 0.328x + 0.011$	0.999
2-Naphthol	DBTHX	$y = 0.520x - 0.169$	0.999
	DBTHP	$y = 0.627x - 0.202$	0.995
	DBTDMHP	$y = 0.426x - 0.017$	0.998
1-Naphthol	DBTHX	$y = 0.657x - 0.234$	0.998
	DBTHP	$y = 0.778x - 0.254$	0.995
	DBTDMHP	$y = 0.520x - 0.035$	0.998
1-Nitronaphthalene	DBTHX	$y = 0.773x - 0.283$	0.998
	DBTHP	$y = 0.920x - 0.265$	0.995
	DBTDMHP	$y = 0.685x - 0.053$	0.998
2-Methoxynaphthalene	DBTHX	$y = 1.01x - 0.358$	0.999
	DBTHP	$y = 1.17x - 0.333$	0.995
	DBTDMHP	$y = 0.938x - 0.105$	0.998
1-Methoxynaphthalene	DBTHX	$y = 1.51x - 0.533$	0.999
	DBTHP	$y = 1.75x - 0.490$	0.994
	DBTDMHP	$y = 1.44x - 0.201$	0.998

value decreases in the order DBTHP > DBTHX > DBTDMHP in both cases. However, the CMC values obtained from the surface-tension plots are about one order of magnitude smaller compared to those estimated from the MEKC plots. The reason for this discrepancy is not clear at present but is speculated as follows. In general, it is unlikely that the discrepancy comes from temperature differences in the tension and MEKC measurements. The presence of salts usually reduces CMC, but the results obtained are not consistent. Since the surfactant molecules in water are partitioned between the bulk phase and the interface, the CMC values are affected by the property of the interface. The surface tension and the MEKC methods are related with the gas–liquid and the solid–liquid interfaces, respectively. In the latter case, adsorption should result in an increased total amount of molecules required to aggregate in the bulk phase as compared with the case of the surface-tension method. Thus, the above-mentioned discrepancy in the CMC values may be ascribed to differences in measurement environment.

The elution order of the analytes in MEKC with the double-chain surfactants is identical, i.e., 1-naphthalenemethanol <1 -naphthylamine <1 -naphthaleneethanol < 2-naphthol < 1-naphthol < 1-nitronaphthalene < 2-methoxynaphthalene < 1-methoxynaphthalene. This elution order is clearly different from that found with SDS, i.e., 1-naphthylamine < 1-naphthalenemethanol < 1-naphthol < 2-naphthol < 1-naphthaleneethanol < 1-nitronaphthalene < 2-methoxynaphthalene < 1-methoxynaphthalene. Namely, the elution order of 1-naphthalenemethanol and 1-naphthylamine as well as that of 1-naphthaleneethanol, 2-naphthol and 1-naphthol was reversed in the SDS system. As already mentioned, 1-naphthalenemethanol, 2-naphthol and 1-naphthol could not be baseline separated in the SDS system, though this was readily done in the double-chain surfactant systems. In HPLC analysis, the 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 found in the double-chain surfactant systems, except that 1-naphthylamine eluted between 2- and 1-naphthol.

A wide migration-time window between t_o and t_{mc} is favorable for high resolution, although a long analysis time may be required. The t_{mc}/t_o value is directly related to the width of the migration-time window. The larger the value of t_{mc}/t_o, the wider the migration-time window. The t_{mc}/t_o values of DBTHX, DBTHP and DBTDMHP at 10 m*M* were 6.0, 5.8 and 4.5, respectively. On the other hand, the value was 4.1 for SDS at 10 m*M*. The double-chain surfactants produced larger t_{mc}/t_o values than SDS at the same concentration. The t_{mc}/t_o value is smaller than 5 for most ionic micelles at pHs greater than 6.0. This is in favor of the use of double-chain surfactants, DBTHX and DBTHP in particular, as micelle-forming reagents in MEKC.

Compared with SDS, the three double-chain surfactants, DBTHX, DBTHP and DBTDMHP, exhibited a remarkably different selectivity of the substituted naphthalene derivatives in MEKC; their MEKC separation could be performed with the double-chain surfactants at concentrations at least one order of magnitude lower. The performance of MEKC separations at low surfactant concentration enables the use of the separation solutions at low ionic strength (low current). This results in a decrease in Joule heating and in a high column efficiency. Moreover, the double-chain surfactants, DBTHX and DBTHP, gave significantly wider migration-time windows. These results suggest that the introduction of double-chain surfactants is promising for MEKC performance. Quite recently, capillary electrophoresis including MEKC has become competitive in trace analysis and the door has been opened to environmental applications in real matrices. The application of double-chain surfactants to the determination of pollutants such as aromatic hydrocarbons in waste gases is of great interest.

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References

[1] S. Terabe, K. Otsuka, K. Ichikawa, A. Tsuchiya and T. Ando, Anal. Chem., 56 (1984) 111–113.
[2] Y.-P. Zhu, A. Masuyama, T. Nagata and M. Okahara, J. Jpn. Oil. Chem. Soc. (Yukagaku), 40 (1991) 473–477.
[3] Y.-P. Zhu, A. Masuyama and M. Okahara, J. Am. Oil. Chem. Soc., 67 (1990) 459–463.
[4] M. Tanaka, T. Ishida, T. Araki, A. Masuyama, Y. Nakatsuji, M. Okahara and S. Terabe, J. Chromatogr., 648 (1993) 469–473.
[5] S. Terabe, K. Otsuka and T. Ando, Anal. Chem., 57 (1985) 834–841.