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Microemulsion electrokinetic chromatographic separation of antipyretic analgesic ingredients

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Abstract

Microemulsion electrokinetic chromatographic (MEEKC) separations of caffeine, aminopyine, phenobarbital and phenacetin were studied using three different core phases. The effects of core phase on migration time and efficiency are discussed. The reproducibility using octane as the core phase is better than that using heptane or 1-butyl chloride. This may be explained in terms of microemulsion stability. Using a microemulsion consisting of 80 m*M* octane–120 m*M* sodium dodecyl sulphate–900 m*M* 1-butanol–10 m*M* borate, the R.S.D. of the migration time was less than 0.8% and that of the peak area was less than 3% ($n = 6$). The effect of core phase concentration on separation was also investigated.

Keywords: Microemulsion electrokinetic chromatography; Capillary columns; Caffeine; Aminopyrine; Phenobarbital; Phenacetin

1. Introduction

Microemulsion electrokinetic chromatography (MEEKC) is an electrokinetic chromatographic method with an oil-in-water (o/w) microemulsion as a separation carrier. The microemulsion (o/w) consists of oil, water, a surfactant and a co-surfactant. Oil, which is named the core phase, usually a hydrocarbon or other hydrophobic substance, is enclosed by the surfactant and the co-surfactant to stabilize oil droplets. Microemulsions have characteristic properties such as optical transparency, thermodynamic stability and high solubilization power. In 1991, Watarai [1] reported the use of an o/w microemulsion composed of heptane–1-butanol–sodium dodecyl sulphate (SDS)–water as a useful medium for the capillary electrophoretic separation of ionic and non-ionic samples. Terabe et al. [2] studied the fundamental characteristics of MEEKC in comparison with micellar electrokinetic chromatography (MEKC). They showed that the separation selectivity of MEEKC may be affected by the character of the core oil (core phase) of the microemulsion.

In this study, three different core phases of microemulsions were employed for the MEEKC separation of antipyretic analgesic ingredients. The reproducibilities of migration times and peak areas were compared. The effect of core phase concentration on migration time is discussed.

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2. Experimental

2.1. Apparatus

Experiments were performed using a Quauta 4000 CE system (Waters, Milford, MA, USA) with a UV detector set at 254 nm. A fused-silica tube of 50 μm I.D, total length 36 cm and effective length 28 cm was used without any special wall treatment. Sample solutions were injected into the end of the capillary by the siphoning method (hydrostatic injection). Electropherograms were recorded with a Chromatopac C-R6A data processor (Shimadzu, Kyoto, Japan).

2.2. Reagents and materials

All reagents were of analytical-reagent grade. Sodium dodecyl sulphate was obtained from Guangzhou Chemical Reagents (Guangzhou, China), heptane, octane, 1-butyl chloride and 1-butanol from Shanghai Chemicals (Shanghai, China) and caffeine, aminopyrine, phenobarbital and phenacetin from Xinhua Pharmaceutical Factory (Shandong Province, China). All solutions were prepared with deionized water. The concentration of each component in the samples ranged from 30 to 300 μg/ml.

2.3. Microemulsion preparation

A microemulsion was prepared by mixing a weighed amount of each component. In most instances, the microemulsion was composed of 80 m*M* core phase–120 m*M* SDS–900 m*M* 1-butanol–10 m*M* borate. The core phase was heptane, octane or 1-butyl chloride.

3. Results and discussion

3.1. Effect of different core phase on MEEKC separation

Using heptane, octane and 1-butyl chloride as the core phase, MEEKC separations of caffeine, aminopyrine, phenobarbital and phenacetin were obtained as shown in Fig. 1. Since the electroosmotic flow was faster than the electrophoretic velocity of the microemulsion, negatively

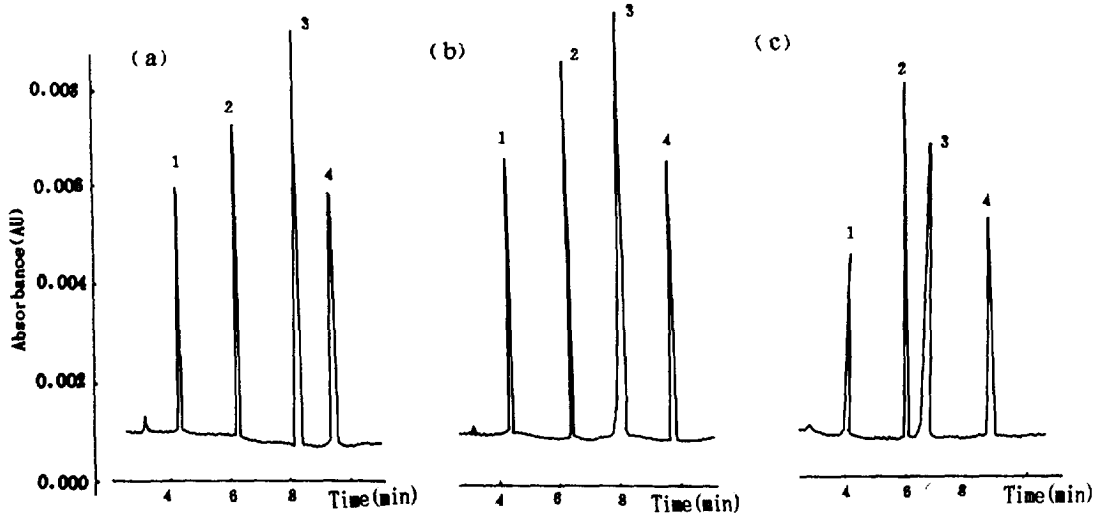

Fig. 1. MEEKC separation of antipyretic analgesic ingredients. MEEKC conditions: capillary, 36 cm (28 cm to the detector) × 50 μm I.D.; applied voltage, 12 kV; current, ca. 65 μA; temperature, ca. 19.5°C; detection wavelength, 254 nm. Separation solution (microemulsion): (a) 80 m*M* heptane–120 m*M* SDS–900 m*M* 1-butanol–10 m*M* borate; (b) 80 m*M* octane–120 m*M* SDS–900 m*M* 1-butanol–10 m*M* borate; (c) 80 m*M* 1-butyl chloride–120 m*M* SDS–900 m*M* 1-butanol–10 m*M* borate. Peaks: 1 = caffeine; 2 = aminopyrine; 3 = phenobarbital; 4 = phenacetin.

Table 1
Comparison of migration times (t) and efficiencies (theoretical plates per metre, N) of different core phases

Core phase	Caffeine		Aminopyrine		Phenobarbital		Phenacetin	
	t (min)	N ($\times 10^4$)	t (min)	N ($\times 10^4$)	t (min)	N ($\times 10^4$)	t (min)	N ($\times 10^4$)
Heptane	4.447	12.3	6.366	25.4	8.314	13.2	9.479	14.2
Octane	4.482	13.2	6.444	21.4	8.158	12.1	9.744	15.3
Butyl chloride	4.115	5.82	5.946	18.1	6.669	5.09	8.860	11.3

Conditions as in Fig. 1.

charged under the given conditions, all the solutes migrated towards the cathode.

Fig. 1 shows that the separation of the four components was achieved within 10 min and the separation efficiency was up to 10^5 theoretical plates per metre (N). The migration times of the solutes depended on the interaction between the solutes and the microemulsions. The more the solute interacted with the microemulsion, the longer was its migration time. The migration time also varied with the core phase. The migration time and efficiency (N) are given in Table 1 for the solutes shown in Fig. 1.

The results in Table 1 and Fig. 1 demonstrate that MEEKC separations using both heptane and octane as the core phase were similar due to the homologues. The migration time using octane as the core phase was slightly longer than that using heptane because the carbon number in octane was one greater than that in heptane. However, both the migration time and efficiency using 1-butyl chloride as the core phase were lower than those using the other core phases. This was attributed to the polarity of 1-butyl chloride. Polar 1-butyl chloride may be partially dissolved in the aqueous phase (consisting of water and 1-butanol), and this may lead to changes in both the distribution coefficient and electroosmotic flow.

3.2. Reproducibility

The reproducibility of migration times and peak areas is critical for quantitative analysis. The precisions of the migration times and peak areas using three different core phases are summarized in Table 2.

Although microemulsions with a heptane core phase were mainly employed by both Watarai [1] and Terabe et al. [2], the results in Table 2 show that the reproducibilities were best using octane as the core phase. This may be explained in terms of the stability of the microemulsion. When the number of carbon atoms in the surfactant molecule is equal to that in the co-surfactant molecule plus that in the oil (core phase) molecule, good microemulsion composition matching is obtained. The carbon number of the surfactant, co-surfactant and core phase conformed with the relationship of the carbon number in the

Table 2
Relative standard deviations of migration times and peak areas ($n = 6$)

Core phase	Caffeine		Aminopyrine		Phenobarbital		Phenacetin	
	Time	Area	Time	Area	Time	Area	Time	Area
Heptane	0.48	4.6	0.56	2.7	0.77	2.9	0.86	5.4
Octane	0.27	1.0	0.42	1.9	0.36	2.0	0.71	2.7
Butyl chloride	0.70	1.9	1.2	1.9	0.99	0.86	1.8	2.2

Conditions as in Fig. 1.

Table 3
Effect of octane concentration on migration time

Octane (m*M*)	Migration time (min)			
	Caffeine	Aminopyrine	Phenobarbital	Phenacetin
0	3.927	5.286	6.622	7.228
40	4.005	5.497	6.816	7.762
80	4.187	5.929	7.489	8.624

Temperature, ca. 20.6°C; other conditions as in Fig. 1.

octane–SDS–1-butanol–borate microemulsion. For this reason, a microemulsion using octane as the core phase may be the most stable.

3.3. Effect of core phase concentration on migration time

The effect of core phase concentration on migration time was investigated. The separation was carried out under the conditions in Fig. 1b except for the octane concentration. The results are given in Table 3. The migration time increased with increase in core phase concentration. The stronger the hydrophobicity of the solute, the more the migration time increased. No changes occurred in the elution order of the solutes.

4. Conclusions

MEEKC is a relatively new capillary electrophoretic technique using a microemulsion as a separation carrier. MEEKC separations are affected by the microemulsion composition, i.e., the core phase, surfactant and co-surfactant. The reproducibility of separation may depend mainly on the stability of the microemulsion. High efficiency can be obtained if the microemulsion composition is properly chosen.

References

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