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Determination of cationic surfactants by capillary electrophoresis with indirect photometric detection

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Abstract

The separation of quaternary alkyl and dialkyl ammonium compounds by capillary electrophoresis has been performed using indirect UV detection. The influence of the organic modifier on the electrophoretic behaviour of the analytes is discussed. Several chromophoric electrolyte constituents, including absorbing cationic surfactants, have been investigated for indirect UV detection. The results of method development are applied to the determination of cationic surfactants in cosmetics and pharmaceuticals. A comparison to high-performance liquid chromatography with respect to efficiency, reproducibility and detection limits is presented. © 1997 Elsevier Science B.V.

Keywords: Surfactants

1. Introduction

Cationic surfactants are widely used in industrial and commercial formulations, including disinfectants, textile softeners, cosmetics and pharmaceuticals [1]. Several analytical methods have been applied for product control and environmental analysis. For the quantitative determination of cationic surfactants photometry [2] or potentiometry [3] have been used. These methods often suffer from interfering substances and require careful sample pretreatment. Furthermore, they do not give any information about homologous or isomeric distribution. Infrared and nuclear magnetic resonance spectrometry (NMR) are used for structural analysis [1]. Mass spectrometry (MS) is very effective for specific and sensitive surfactant analysis [4]. Gas chromatographic (GC) separation of quaternary ammonium compounds requires derivatization [5]. High-performance liquid chromatography (HPLC) is the most promis-

ing and convenient technique for the determination of cationic surfactants in industrial and environmental samples [6–8]. Capillary electrophoresis (CE) has been increasingly applied for the analysis of anionic surfactants [9–12], whereas cationics are only rarely investigated. The addition of organic solvents like tetrahydrofuran (THF) [13,14], methanol [15], acetonitrile or acetone [16,17] has been used to prevent adsorption onto the capillary wall and micelle formation, leading to peak tailing and insufficient separation efficiency. For indirect UV detection of non-chromophoric quaternaries dodecylbenzyltrimethylammonium chloride [13], pyridine, benzylamine [15] or rhodamine [18] were used as absorbing electrolyte components. A determination of cationic surfactants in commercial products has been described by Weiss et al. [13].

This paper presents the separation of homologous alkyl and dialkyl ammonium compounds by CE with indirect photometric detection. The influence of organic solvents as well as absorbing electrolyte components has been examined. Cetrimonium bro-

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mide was determined in a face lotion; HPLC was used as reference method.

2. Experimental

2.1. Apparatus

2.1.1. Capillary electrophoresis

CE was performed on a P/ACE 2100 system (Beckman), monitored by an IBM personal computer (PC) using GOLD software (Beckman). Injections (at the anodic end) were performed in the pressure mode and the injection time was set at 5 s. Fused-silica capillaries of 57 cm (50 cm to the detection window) \times 75 μ m I.D. were used (Chromatographie Service, Langerwehe). The UV detector was set at 214 nm, operation voltage was 20 kV.

2.1.2. High-performance liquid chromatography

A Beckman System Gold consisting of a Model 126 programmable solvent module, an injection valve with 20 μ l loop and a Model 168 diode array detector module was used. Data acquisition was performed on an IBM PC with Beckman System Gold software. The column thermostat (set at 25°C) was from WO Electronics (Austria). The detector was set at 254 nm. Separations were performed on a C₈ column, 250 \times 4 mm (Beckman) with 5 mmol/l benzyltrimethylammonium chloride in acetonitrile–0.02 mol/l HCl (70:30) with a flow-rate of 1 ml/min.

2.2. Chemicals

Benzyltrimethylammonium chloride, creatinine, imidazole, aminobenzimidazole were obtained from Sigma (Deisenhofen, Germany). Dodecyl-, tetradecyl- and hexadecylbenzyltrimethylammonium compounds (alkylbenzyl-DMA), dodecyl-, tetradecyl-, hexadecyl and octadecyltrimethylammonium bromides (alkyl-TMA) and didodecyl-, ditetradecyl-, dihexadecyl- and dioctadecyltrimethylammonium bromides (dialkyl-DMA) were from Fluka (Neu-Ulm, Germany). Na₂HPO₄ and NaH₂PO₄ buffer substances, HCl, sodium dodecyl sulfate (SDS) were from Merck (Darmstadt, Germany). Organic solvents for CE (acetonitrile, acetone, methanol, ethanol,

THF, 2-propanol) were obtained from Merck. Acetonitrile of HPLC grade was from Roth (Karlsruhe, Germany). All solutions were prepared using Milli-Q water. The pH values of the electrolytes were adjusted in the stock solutions (100 mmol/l) before adding organic solvents.

The face lotion "Clearasil" (Procter and Gamble, Schwalbach, Germany) was diluted 1:4 (for HPLC) or 1:10 (for CE).

3. Results and discussion

3.1. Capillary electrophoresis

3.1.1. Influence of organic modifiers

The ability of cationic surfactants to sorb onto the capillary surface and to form micelles at low concentrations is the reason for peak tailing and insufficient resolution in CE. Other problems are their low solubility in pure aqueous solution and the small differences in electrophoretic mobilities of long-chain homologues. The use of organic solvents as electrolyte additives in the electrophoretic determination of cationic surfactants is essential to obtain efficient separations. The influence of different organic solvents has been examined for the separation of alkyl-TMA using indirect UV detection with benzyltrimethylammonium chloride (BTMAC) as chromophore (Fig. 1). According to their different viscosities and dielectric constants organic modifiers influence the electroosmotic flow (EOF) and therefore the electrophoretic behaviour of cationic surfactants. The migration time and peak resolution is increased with increasing viscosity and decreasing dielectric constant of the organic solvent. Acetonitrile (A) and acetone (F) exert the slightest influence on the EOF, leading to short migration times, sharp peaks but insufficient peak resolution. With 2-propanol (D) the greatest effect on migration times could be observed, but without improvement of peak resolution. The addition of methanol (B) was not found to be useful because it produces a strong baseline noise. With THF (E) an effective separation according to baseline peak resolution and peak shape could be obtained, therefore it was chosen as organic modifier for the further investigations. The separation efficiency can be improved by increasing the

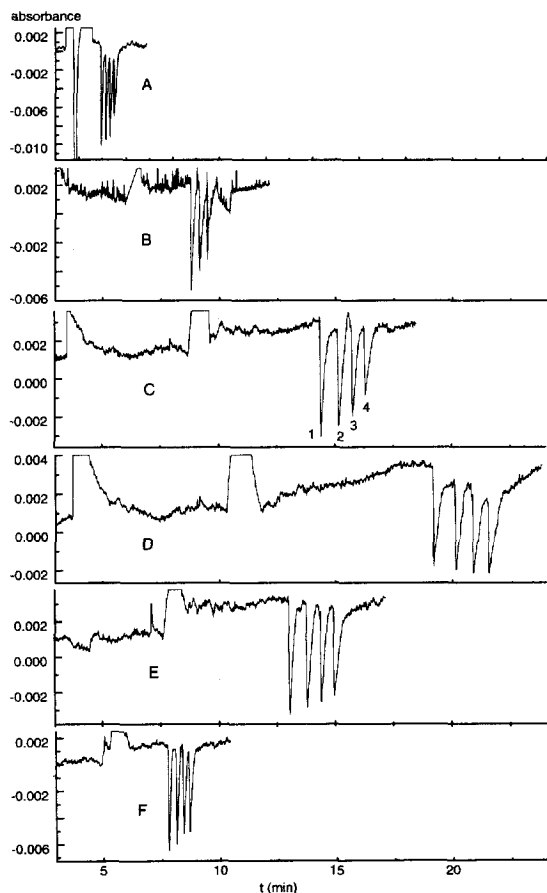


Fig. 1. Separation of alkyl-TMA in various organic solvents: (A) acetonitrile, (B) methanol, (C) ethanol, (D) 2-propanol, (E) THF, (F) acetone, (1) C_{12} , (2) C_{14} , (3) C_{16} , (4) C_{18} -TMA. 20 mmol/l phosphate pH 4.4, 40% acetonitrile, 5 mmol/l BTMAC.

organic content in the electrolyte, due to its influence on the EOF via viscosity and dielectric constant. An increase in electrolyte concentration leads to a decrease of the zeta-potential and therefore of the EOF; migration times and peak resolution are increased. The increase of electrolyte and solvent concentration is limited by the miscibility and the increasing baseline noise. Furthermore, a decrease of pH leads to a lower dissociation of the silanol groups of the capillary surface and therefore to a reduced EOF and also a reduced adsorption of cationic surfactants on the negatively charged wall. Low sample concentrations and an organic content in the

sample [17] are other important facts for a good peak resolution.

3.1.2. Influence of electrolyte chromophore

Because the investigated cationic surfactants do not possess any chromophoric groups, indirect photometric detection with chromophoric cations in the electrolyte has been performed. The best detection sensitivity is obtained with a high UV absorbance and a low concentration of the UV-background electrolyte [19]. Furthermore, the absorbing electrolyte component should have a similar mobility like the analyte. Various organic cationic substances have been tested to find the conditions for an efficient separation. Fig. 2 presents a comparison of the separations of alkyl-TMA in creatinine (A), imidazole (B) and aminobenzimidazole (C) and in a phosphate electrolyte containing BTMAC (D). The differences in electrophoretic mobilities of the slowly moving surfactants and faster moving absorbing electrolyte components led to a peak tailing. The best peak shape was observed with BTMAC, the strongest tailing with imidazole. The optimum pH has been determined for imidazole to be about 4.5. The addition of SDS was necessary for the improvement of peak resolution due to the formation of ion pairs with the analytes. But it led also to peak broadening, increasing baseline noise and decreasing signal intensity. The best compromise was a SDS concentration of 3 mmol/l (determined with BTMAC-electrolyte).

In order to improve the peak shape, alkylbenzylammonium compounds have been used as chromophores. Fig. 3 shows a comparison of alkyl-TMA separations in C_{12} -, C_{14} - and C_{16} -benzyl-DMA containing electrolytes. The optimum peak symmetry of alkyl-TMA changes from C_{14} (A) to C_{16} (B) and C_{18} (C). After adding 40% THF a sufficient peak resolution without SDS could be achieved. Acetonitrile was not suited because of the overlapping of the C_{12} -TMA peak with a system peak.

The separation of long-chain dialkyldimethylammonium compounds is difficult because of their low electrophoretic mobility and high tendency to form micelles and to sorb onto the capillary surface. For the separation of these compounds a higher concentration of organic solvent was necessary. Suf-

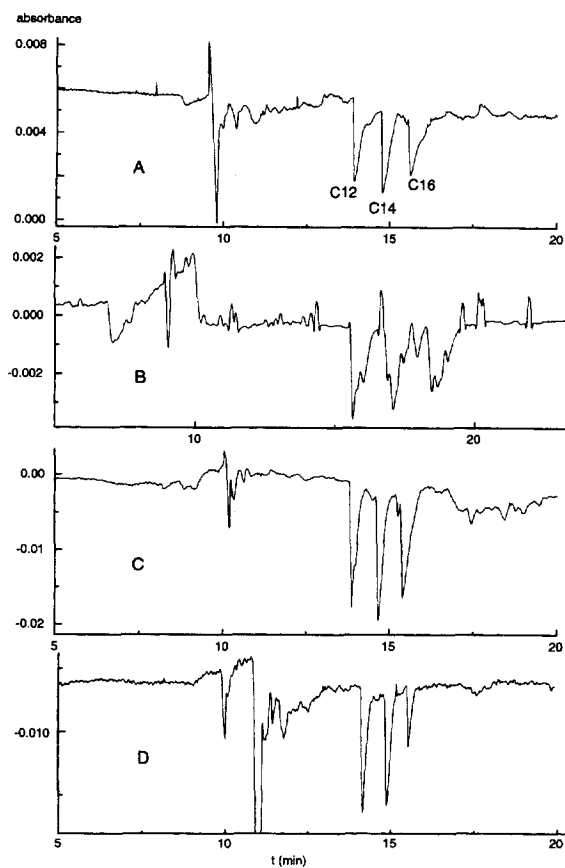


Fig. 2. Comparison of cationic electrolytes for indirect UV detection of alkyl-TMA: (A) creatinine, (B) imidazole, (C) aminobenzimidazole, (D) BTMAC. A–C: 5 mmol/l electrolyte pH 4.5, 50% THF, 3 mmol/l SDS, D: 5 mmol/l BTMAC in 50 mmol/l phosphate pH 6.8, 50% THF, 3 mmol/l SDS.

cient peak resolution of alkyl-TMA and dialkyl-DMA (Fig. 4) could be achieved using 50% THF. A further increase of the organic content led to increasing baseline noise. The dioctyl-DMA could not be separated from the dihexadecyl-DMA because of low solubility, lower critical micelle concentration and low differences in the electrophoretic mobilities.

3.2. Comparison to HPLC

In HPLC, ion pairing with HCl was used for the separation of cationic surfactants. The non-absorbing alkyltrimethylammonium compounds have been analyzed using benzyltrimethyl ammonium chloride as

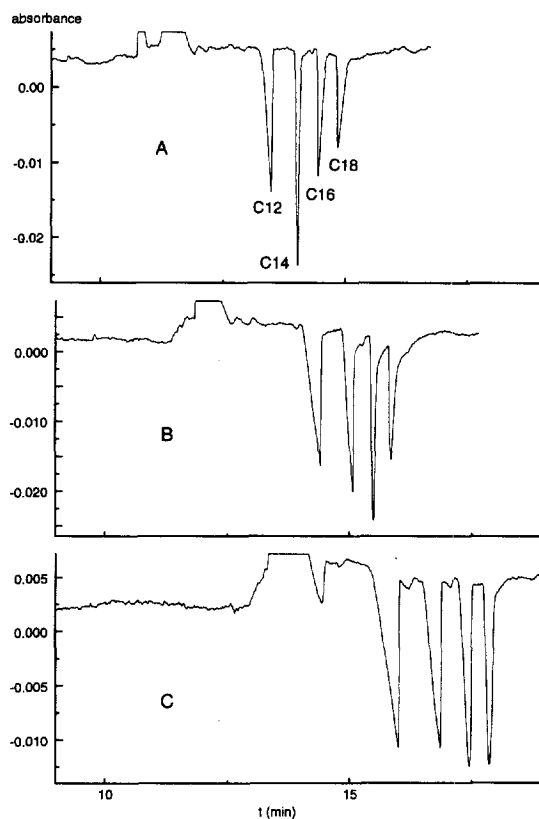


Fig. 3. Separation of alkyl-TMA using alkylbenzyl-DMA as chromophores: (A) C₁₂, (B) C₁₄, (C) C₁₆-benzyltrimethylammonium chloride. 5 mmol/l chromophore, 20 mmol/l phosphate pH 4.4, 40% THF.

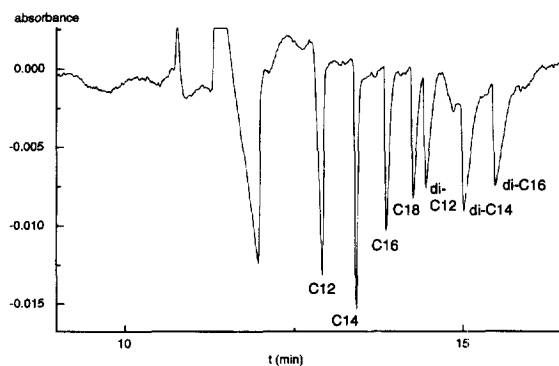


Fig. 4. Separation of alkyl and dialkyl quaternary ammonium compounds. 5 mmol/l C₁₂-benzyl-DMA, 20 mmol/l phosphate pH 4.4, 50% THF.

chromophoric background for indirect UV detection. A comparison of CE and HPLC with respect to detection limits and reproducibility is presented in Table 1 investigating the C₁₄-alkyl homologue. In general, HPLC is characterized by lower detection limits and better reproducibility than CE. That is correct for direct UV detection of cationic surfactants, whereas in the indirect mode with both methods similar detection limits could be obtained. The increased sensitivity in CE results from the good peak shape (same mobilities of absorbing component and sample) and the decreased sensitivity in HPLC from peak tailing. The application of suppressed conductivity detection in HPLC is an alternative technique to obtain better efficiency and sensitivity [7]. CE can be considered as a complimentary method to HPLC for the analysis of cationic surfactants; with the advantages of minimal solvent consumption, higher efficiency, easy cleaning and inexpensive replacement of columns and the ability for a fast method development by changing the electrolyte composition. The analysis of complicated sample matrices without pretreatment is possible.

3.3. Application

Cetrimonium bromide, applied in face lotion because of its antiseptic properties, has been identified as C₁₄-TMA bromide and determined by external calibration (see Table 1) to be 5.62 g/l (Fig. 5B). HPLC analysis (Fig. 5A) yields a content of 5.69 g/l. For the electrophoretic separation, C₁₂-benzyl-DMA has been chosen as background chromophore because of the best congruence of the electrophoretic mobilities leading to a very sharp peak. In HPLC, BTMAC was chosen because with alkylbenzyl-DMA no useful results could be obtained, due to a strong

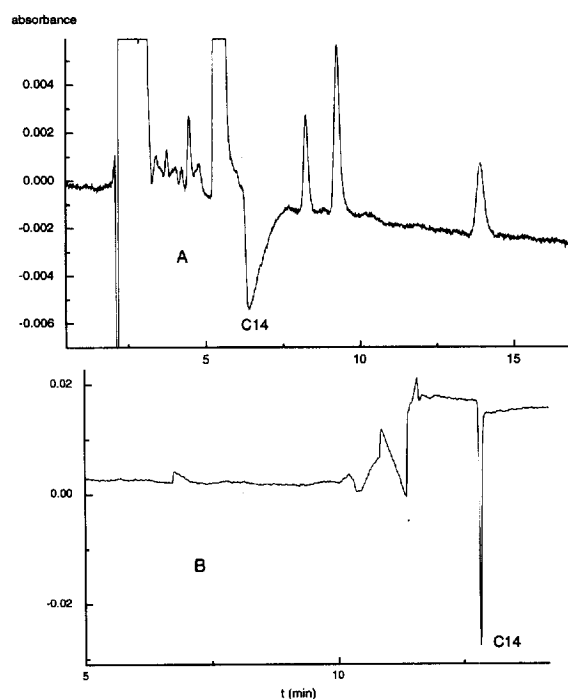


Fig. 5. Analysis of cetrimonium bromide in face lotion by (A) HPLC and (B) CE, conditions see Fig. 3A.

interaction of the electrolyte surfactant with the stationary phase.

4. Conclusions

Homologous separations of cationic surfactants could be achieved using high contents of organic solvents. THF was found to be well suited for a sufficient peak resolution. Alkylbenzyl-DMA compounds are effective background chromophores to separate alkyl and dialkyl quaternary ammonium

Table 1
Comparison of HPLC and CE for the determination of C₁₄-TMA

	HPLC (conditions as in Section 2.1.2)	CE (conditions as in Fig. 5B)
Correlation coefficient	0.9989	0.9989
Limit of detection (mol/l)	$2.1 \cdot 10^{-5}$	$1.6 \cdot 10^{-5}$
Reproducibility (R.S.D., %)	1.07	5.80

compounds. The developed method was found to be useful for the analysis of commercial samples.

Acknowledgments

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