

Analysis of cationic surfactants by capillary electrophoresis

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Abstract

Capillary zone electrophoresis was applied to the analysis of N-benzyl-N-alkyl-N,N-dimethylammonium chloride compounds with different alkyl chain lengths (C_{12} – C_{18}) by direct UV detection. A tetrahydrofuran-containing buffer was used to prevent the occurrence of micellization and adsorption of the surfactants, thereby yielding adequate separations according to their free-form electrophoretic mobilities. Resolution, theoretical plate number, reproducibility and precision were ascertained. Finally, the electrophoretic method was applied to the qualitative and quantitative determination of an industrial mixture of C_n -benzyl surfactants.

Keywords: Quaternary ammonium compounds; Surfactants; N-Benzyl-N-alkyl-N,N-dimethylammonium chloride

1. Introduction

Cationic surfactants are important additives in many chemical processes and formulations. They are commonly used as antimicrobial, emulsifying, anticorrosion and softening agents in detergent formulations, textile materials and human hair cosmetics [1].

It is necessary to develop appropriate and accurate analytical techniques for the separation and detection of cationic surfactants in order to monitor production, formulation, application and, more interestingly, to control the residual liquors and effluents. The qualitative and quantitative determination of cationic surfactants has usually been performed by traditional and widely used methods, i.e., two-phase titration [2,3], high-performance liquid chromatography (HPLC) [4–6], gas chromatography (GC) [7–9] and thin-layer chromatography (TLC) [10–13]. How-

ever, complete characterization is sometimes difficult, given the problems associated with the strong sorption and incomplete separation of these cationic compounds.

Although there are a small number of papers on the analysis of ionic surfactants, the results described so far on this subject indicate that capillary electrophoresis (CE) is a promising technique for the separation and quantification of a wide class of compounds differing by only one carbon atom in the alkyl chain [14–21]. The successful application of CE in this field requires that the surfactant migrates freely through the column, with minimum adsorption and aggregation and suitable spectroscopic characteristics to detect the compound during the migration process. Organic modifiers such as methanol [17,18], acetonitrile [18,19,21] and tetrahydrofuran (THF) [16,17] have been introduced in the CE-buffer system in order to disrupt micelle formation within the sample and to reduce the ability of surfactants to sorb strongly onto capillary walls.

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In this paper, a systematic investigation of the operational buffer systems and instrument parameters to achieve the best possible performance for the separation and quantification of an homologous series of *N*-benzyl-*N*-alkyl-*N,N*-dimethylammonium chloride compounds (C_{12} – C_{18}) by capillary zone electrophoresis (CZE) with direct UV-detection is reported. Almost all of the experiments were carried out in a bare silica capillary that was filled with a phosphate buffer in water–THF. Statistical analysis of the results is carried out. A cationic mixture of industrial interest is analyzed.

2. Experimental

2.1. Chemicals

The following conventional cationic surfactants were supplied by Aldrich (Milwaukee, WI, USA): *N*-benzyl-*N*-dodecyl-*N,N*-dimethylammonium chloride (C_{12} -benzyl), *N*-benzyl-*N*-tetradecyl-*N,N*-dimethylammonium chloride (C_{14} -benzyl), *N*-benzyl-*N*-hexadecyl-*N,N*-dimethylammonium chloride (C_{16} -benzyl), *N*-benzyl-*N*-octadecyl-*N,N*-dimethylammonium chloride (C_{18} -benzyl), all of which were of pro-analysis grade.

An industrial mixture of C_n -benzyl surfactants was generously supplied by Kao Corporation (Barcelona, Spain). This was a 50% (w/w) water solution containing a mixture of C_{12} – C_{14} benzyl (70:30, w/w) with traces of C_{16} -benzyl. This sample and the pure surfactants were diluted in ultrapure deionized water prior to analysis.

All of the buffer systems and washing solutions were prepared from ultrapure deionized water produced by a Millipore Milli-Q system and from the highest available grades of the following analytical reagents: Citric acid monohydrate, sodium hydroxide, hydrochloric acid in water solution (25%), disodium hydrogenphosphate dihydrate, and tetrahydrofuran (THF), supplied by Merck, and sodium dihydrogenphosphate dihydrate supplied by Fluka, all of which were of pro-analysis grade and used without any further purification.

THF-containing buffers were prepared by first dissolving the appropriate mass of buffer salts in the appropriate volume of water. Then, the aqueous pH

electrolyte solution was measured using a classic pair of glass reference electrodes. The terminating buffer solutions were prepared simply by mixing the appropriate volume of THF in the aqueous electrolyte solutions. All buffers and washing solutions were filtered through a 0.22- μ m membrane filter from Millipore.

2.2. Equipment

The separations were performed with an Applied Biosystems Model 270A (Foster City, CA, USA) apparatus which consisted of the following functional assemblies; a controller, the sample (at the beginning) and the detector (at the end) electrode compartments, an UV–Vis detector compartment, an autosampler assembly and a capillary oven. A single type column of uncoated fused-silica was used (72 cm \times 50 μ m I.D.), which was obtained from Composite Metal Services (Worcs., UK). The distance between the sample injection and the detector was 51 cm. The new column was conditioned by treating it with 1.0 *M* NaOH for 20 min and with water for 3 min. During routine analysis, the capillary columns were washed with 0.1 *M* NaOH for 5 min and rinsed with buffer. All of these procedures were done by applying a vacuum to the detector electrode reservoir for a specified time. Sample introduction was achieved by the same system. The separation unit was equipped with a UV absorbance detector operating at 210 nm throughout the analyses. The signals were recorded on a Shimadzu C-R6A Chromatopac chart recorder coupled to the CE instrument.

All analyses were performed in the following stages: The capillary column was washed with 0.1 *M* NaOH for 5 min and rinsed with buffer for 5 min. Then the appropriate volume of sample mixture was injected into the column, after which a high voltage (15–30 kV) was applied. The analysis time varied between 5–30 min, depending on the sample. During the separation process, the capillary column was thermostated between 30–35°C. The attenuation chart recorder was set at 5 mV/full scale in all the analyses.

In all of the analyses, the cathode was situated at the detector end of the capillary, whereas, the anode was at the sample injection end.

3. Results and discussion

3.1. Qualitative aspects

Initial attempts to separate the N-benzyl-N-alkyl-N,N-dimethylammonium chloride series were performed in aqueous media without the use of organic modifiers. Two different phosphate buffers were used: (a) 12.25 mM $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, 28.125 mM $\text{Na}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, pH 6.5, in water and (b) 0.05 M $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, pH 4.5, in water. Surfactant concentrations in the samples were 1 mM.

These cationic compounds were expected to elute from the capillary column in order of decreasing charge-to-mass ratio, i.e., in order of increasing alkyl chain length. The signal obtained for the C_{12} -homologue was acceptable, with a retention time of 5.0 min. However, although the signal for the C_{14} -benzyl homologue appeared at 5.3 min, it was broad, asymmetric and tailing. No signals were obtained for the C_{16} - and C_{18} -benzyl compounds. The influence of the chain length of the surfactant in peak tailing or even in peak loss has also been observed in a series of alkyl sulfates (C_8 – C_{18}) [18] and by Weiss et al. [16] in the same homologue series of alkylbenzyl dimethyl ammonium halide compounds (C_{12} – C_{18}). In line with these authors, these effects, which worsened with increasing chain length, could be due to the formation of micelles in the buffer system [16] and/or to the hydrophobic adsorption of these surfactants on the capillary wall [18]. Although precipitation of the longer chain surfactants has also been proposed to account for this phenomenon [18], no precipitation was detected in the present study, either in the column or in the sample solutions. We determined the critical micelle concentrations (CMCs) for these compounds in an aqueous 0.05 M $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ solution by plotting the equilibrium surface tension values versus the log surfactant concentration following the Wilhelmy plate method. The data are given in Table 1. It should be noted that the concentration of the solutions introduced into the CE column were of the order of 1 mM, which would indicate that the C_{12} -benzyl compound could be in the CE system at a concentration around its CMC. The C_{14} -, C_{16} - and C_{18} -benzyl compounds were introduced at a level of one, two and three orders of magnitude above their CMC, respectively, and they

Table 1

CMC of N-benzyl-N-alkyl-N,N-dimethylammonium chloride compounds in 0.05 M $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, pH 4.5

Compound	CMC (M)
C_{12} -benzyl	$2.6 \cdot 10^{-3}$
C_{14} -benzyl	$2.6 \cdot 10^{-4}$
C_{16} -benzyl	$6.0 \cdot 10^{-5}$
C_{18} -benzyl	$3.0 \cdot 10^{-6}$

could therefore be present in the analysis medium as micelles.

In order to demonstrate the role of the micelles in the peak performance, a series of samples containing increasing concentrations of C_{12} from $0.5 \cdot 10^{-3}$ to $1 \cdot 10^{-2}$ M (above and below its CMC) in an aqueous 0.05 M $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ solution were analyzed. In all cases, the quality of the peaks was excellent and the peak areas linearly increased with increasing concentrations of C_{12} surfactant. Peak tailing was not observed even at a concentration of about $1 \cdot 10^{-2}$ M. Therefore, the observed peak tailing and peak loss in the longer homologues could be largely attributed to the hydrophobic adsorption to the capillary walls, which increased with increasing alkyl chain length [20].

The addition of some commonly used solvents, such as methanol or acetonitrile, was tried but did not result in an improvement in peak performance. According to the findings of Weiss et al. [16], the addition of THF resulted in an improvement in peak shape. However, THF, in our CE buffer system, attacked some acrylic plastic parts in the capillary-end reservoir. More importantly, despite the fact that the buffer solution was an electrical conductor, the electrophoresis instrument display indicated that there was no current across the column in the presence of this organic solvent (50% THF).

In order to overcome this intrinsic limit of our CE apparatus (sensitivity to THF in one compartment and the absence of current when THF was added to all buffer systems), an alternative experimental procedure was tried, i.e., the buffer containing THF was placed only into the glass vial at the injecting end of the capillary column, whereas an aqueous buffer solution at the same electrolyte concentration, but without THF, was placed in the acrylic plastic buffer reservoir at the waste-end of the column. Consequently, current was detected (5 μA at 20 kV) and

adequate separation of all the N-benzyl-N-alkyl-N,N-dimethylammonium chloride compounds was obtained using this strategy. Another alternative consists of replacing the acrylic reservoir by a glass one, as described by Shamsi and Danielson [17].

In accordance with this methodology, the following operating conditions were optimized: the water-THF ratio, the pH of the buffer system, the applied voltage and the sample injection time. The suitability of this strategy was assessed on the basis of resolution, theoretical plate number, reproducibility and precision. The best results were obtained by using water-THF (50:50) containing 0.05 M $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, pH 4.0, at 20 kV of applied voltage and with an injection time of 2 s. As shown in Fig. 1, the peak shapes are good, providing adequate separation of the N-benzyl-N-alkyl-N,N-dimethylammonium chloride compounds. Peak migration times were longer than those reported by Weiss et al. [16]. However,

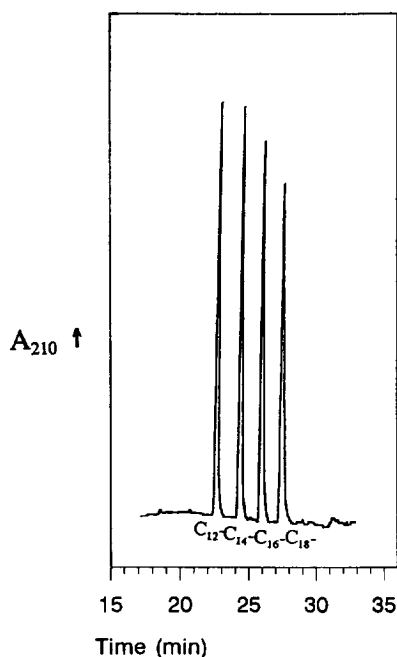


Fig. 1. Electropherogram of an aqueous mixture of C_{12} -, C_{14} -, C_{16} - and C_{18} -benzyl (in order of appearance), each at a concentration of $4 \cdot 10^{-4}$ M, using water-THF (50:50) containing 0.5 M $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, pH 4, at 20 kV and with an injection time of 2 s, on a 72 cm \times 50 μm I.D. column.

the migration time differences between adjacent peaks were improved, providing higher resolution.

The reproducibility of the method was tested prior to studying the quantitative aspects. Fig. 2 shows the variation in migration time versus sample concentration for the four compounds. The results obtained suggest that the migration time of the assayed compounds does not change significantly with the concentration of the sample, at least in the range $0.56\text{--}5.00 \cdot 10^{-4}$ M.

The inter-day reproducibility of migration time, peak area and peak height, for each of the compounds, was also demonstrated.

3.2. Quantitative aspects

The quantitative aspects of the method were studied by injecting various samples of the pure compounds at different concentrations using the aforementioned conditions. The linear relationship between peak area and peak height versus sample concentration was confirmed for the four compounds. The linear relationship was rather better and more sensitive for peak area than for peak height for C_{12} -, C_{14} - and C_{16} -benzyl, whereas for C_{18} -benzyl the relationship was apparently better for peak height, at least at low concentrations. Therefore, technique precision and studies on the quantification limit were done only by peak-area measurement for

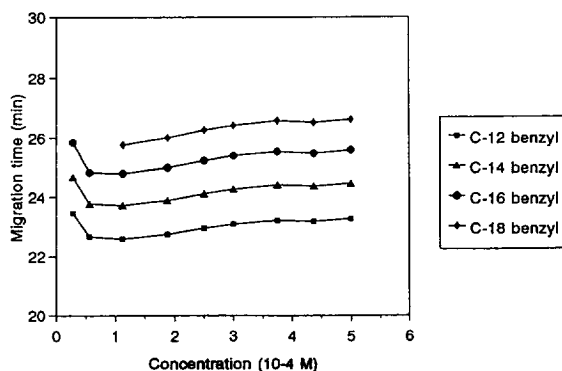


Fig. 2. Migration times for each of the four compounds at different concentrations values, using water-THF (50:50) containing 0.5 M $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, pH 4, at 20 kV and with an injection time of 2 s, on a 72 cm \times 50 μm I.D. column. Each point corresponds to the average of nine analyses.

the C₁₂- to C₁₆-benzyl compounds and by peak-height measurement for the C₁₈-benzyl compound. While the detection limit for these compounds was 1·10⁻⁵ M (around 4 ppm, on average), the quantification limit was estimated to be 0.3·10⁻⁴ M for C₁₂- and C₁₄-benzyl, 0.56·10⁻⁴ M for C₁₆-benzyl and 2·10⁻⁴ M for C₁₈-benzyl. A non-linear relationship was obtained below these quantification limits. The technical precision estimated by calculating the mean value of the recovery (%) for three different measurements and the variation coefficient, at two different concentration levels, for each of the compounds was satisfactory.

The electrophoretic analytical method was applied under the same experimental conditions to the qualitative and quantitative determination of an industrial mixture of C_n-benzyl surfactants, which consisted of a 50% (w/w) water solution containing a mixture of C₁₂-C₁₄ benzyl (70:30, w/w) with traces of C₁₆-benzyl.

Fig. 3 shows the electropherogram obtained. Three different analytes were detected and assigned to C₁₂-, C₁₄- and C₁₆-benzyl homologues. A C₁₈-benzyl homologue was not detected, even at higher concentrations. The concentration of the surfactant mixture that was found, 49.6%, is in agreement with the manufacturer's specification.

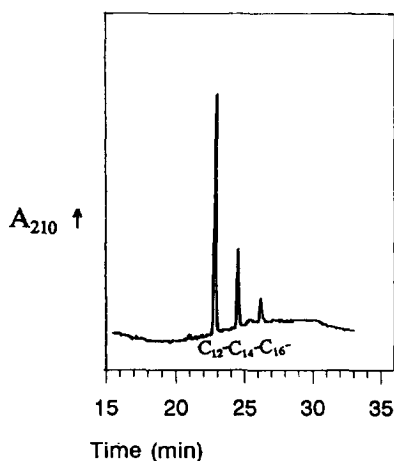


Fig. 3. Electropherogram obtained for the industrial sample, using water-THF (50:50) containing 0.5 M NaH₂PO₄·2H₂O, pH 4, at 20 kV and with an injection time of 2 s, on a 72 cm×50 μm I.D. column.

4. Conclusions

The separation of N-benzyl-N-alkyl-N,N-dimethylammonium chloride compounds (C₁₂-, C₁₄-, C₁₆- and C₁₈-benzyl) was accomplished using CZE with direct UV detection. The addition of THF to the buffer system (except in the acrylic buffer compartment, which contained only aqueous buffer) was carried out to overcome the difficulty arising from adsorption to the capillary wall of these analytes during the course of the analyses. This method was used to determine these compounds in an industrial surfactant mixture sample.

On the basis of the results obtained here, CE could be applied to analyse, both qualitatively and quantitatively, new synthetic cationic surfactants of Gemini type, derived from amino acids. Work is currently in progress in this regard.

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