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Short communication

Isotachophoretic separation of cetyltrimethylammonium bromide

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Abstract

Capillary isotachophoresis (ITP), equipped with the conductivity detection, was tested for the separation of cetyltrimethylamonium (CTMA) bromide. To prevent adsorption of CTMA to the capillary walls, several neutral polymers and ethanol were added into the leading electrolytes. Unlike polymer additives, the CTMA free monomers and micelles, created as a result of the isotachophoretic concentration effect, were recognised in the presence of ethanol from 10 to 25% (v/v). At 30% of ethanol, only a single zone of CTMA monomer was registered because the micellization process did not take place under this condition.

Employing an ITP apparatus in the column-coupling configuration, the operational system with 30% of ethanol was tested for the determination of CTMA in hair conditioners. The achieved detection limits were about 0.02 mM. Both model solutions and real samples of hair conditioners were analysed with the precision about R.S.D. = 3%. One analysis in the column-coupled system takes circa 15 min.

Keywords: Capillary isotachophoresis; Cetyltrimethylammonium bromide; Cationic surfactants; Micelles

1. Introduction

Cationic surfactants, well-known as antibacterial compounds, are introduced into the environment as a part of cleaning products, pharmaceutical preparations, cosmetic formulations and others [1]. Since they have detrimental effects on water organisms, it is desirable to remove them by, e.g. retention on various sorbents.

Clay minerals have layered structures which allow them to be intercalated by quarternary alkylammonium salts [2] including cationic surfactants [3]. These organic cations are fixed on the clay surface by ion-exchange reactions. Moreover, the surfactant hydrophobic chains modify hydrophilic inorganic layers forming materials suitable for the adsorption of various organic compounds [3-5] and also inorganic oxyanions as it has been reported recently [6]. It follows from these facts that clays should be promising sorbents for the removal of cationic surfactants from, e.g. industrial and surface water.

The usual methods for the determination of cationic surfactants are ion-association titration [7], extraction spectrometry [8], high performance liquid chromatography with reversed [9,10] and ion-pair normal phase [11], ion-selective electrode [12] and capillary zone electrophoresis [13,14]. The application of capillary isotachophoresis for the separation of C8–C20 cationic surfactants has already been reported in two papers by Tribet et al. in 1992 [15,16]. Since that time, no other reports on this subject have been published in literature.

The primary aim of this work was to develop a rapid, easy, and reliable ITP method for the study of cationic surfactant sorption on clay materials from the aqueous environment. The ITP experiments were performed with CTMA as a typical cationic surfactant. During the method preparation, some interesting aspects of the surfactant isotachophoresis were found and they are presented in this communication. The proposed ITP method was verified by the determination of CTMA in various cosmetic s formulations.

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2. Experimental

2.1. Reagents

All chemicals were of analytical reagent grade: potassium hydrogen carbonate, sodium chloride, glacial acetic acid, ethanol 99% (all from Lachema, Czech Republic), β-alanine (Serva, Germany), cetyltrimethylammoniu bromide (Sigma, USA). Hydroxyethylcellulose Cellosize-WP-40, polyvinylalcohol 72,000, polyvinylpyrrolidone K 30 (Mr 40,000) (all from Fluka Chemie AG, Switzerland). Twice distilled and deionised water by a mixed-bed ion-exchanger was used for preparation of all solutions.

2.2. Apparatus

A CS Isotachophoretic Analyzer ZK 01 (Villa-Labeco, Spišská Nová Ves, Slovakia) designed for column-switching was used. The capillaries were made of fluorinated ethylene-propylene copolymer and equipped with contact conductivity detectors: a pre-separation capillary 160 mm × 0.8 mm i.d. and an analytical capillary 160 mm × 0.3 mm i.d. The separation of model solutions were performed in the analytical capillary. The real samples were analysed in the column-coupling configuration. When using a single analytical capillary, the driving current was kept at 35 μA. The separations in the coupled capillaries were carried out at the driving current of 150 μA in the pre-separation capillary and 20 μA in the analytical capillary. Samples were injected through a 30 μl sampling loop. The pH values of the operational systems were measured with a pH metre WTW InoLab (Weilheim, Germany).

2.3. Computer simulations and data treatment

Computer isotachophoretic simulations were performed by the SIMUL programme (version 4.0) which is freely available on the website of the Department of Physical and Macromolecular Chemistry, Charles University in Prague. This programme uses the mathematical model described in a paper by Schwer et al. [17].

Isotachopherograms were recorded and evaluated by employing the chromatographic programme CSW 1.7 (DataApex, Ltd., Prague, Czech Republic). All calculations were made at the α = 0.05 significance level by the programme QC. Expert 2.5 (Trilobyte Statistical Software, Ltd., Pardubice, Czech Republic).

3. Results and discussion

3.1. Selection of ITP electrolytes

In general, surfactants mostly consist of one or two long hydrophobic tails and a hydrophilic headgroup. At concentrations greater than the so-called critical micelle concentration (CMC), they form large units of associated surfactants, micelles, containing approximately 50–100 molecules. The published CMCs of CTMA vary from 0.7 to 1.6 mM depending on counter ions and techniques used for their measurements [15,18,19].

Table 1
Composition of ITP electrolytes with no additives

Parameter	Leading electrolyte	Terminating electrolyte
Cation	Potassium	β-alanine
Concentration	5 mM	5 mM
Counter ion	Acetate	Acetate
pH	4.5	4.0
Solvent	Water	Water

The first tested operational system in this work (Table 1) was adopted from Tribet et al. [15]. In addition, to prevent the adsorption of CTMA onto the capillary surface, some non-ionic polymers were added into the leading electrolytes. For this purpose, polyvinylalcohol (PVA), polyvinylpyrrolidone (PVP), and hydroxyethylcellulose (HEC) were used because they are well-known to effectively decrease the ζ-potential of the capillary walls [20]. Sodium, coming from chemicals and laboratory glassware, was utilised as a natural mobility marker.

3.2. ITP migration of CTMA

The concentration of CTMA in the ITP zone was calculated at 2.07 mM when its mobility of $u = 21.7 \times 10^{-9}\ m^2\ V^{-1}\ s^{-1}$ [15] was used for the simulations by the SIMUL programme. At this concentration, the micelles should be created in a solution of CTMA monomers according to the micellization equilibrium. Therefore, the ITP separation of both surfactant states were expected similarly as it was described in the case of anionic surfactants [21,22]. As conductivity measurements are currently used for the CMC determination, the conductivity detection was considered to be useful for their resolution.

However, applying no polymer additives as well as PVA (up to 0.3%), and PVP (up to 0.6%) in the leading electrolytes, no zones of CTMA were registered, likely, due to the full adsorption of CTMA onto the surface of separation compartment. Conversely, in the presence of HEC, two zones, supposed to be surfactant forms, were found in the ITP records (Fig. 1).

In the previous works [15,16], the ITP migration of CTMA micelles was proved by the UV detection of the neutral dye (cerol orange) co-migrating in their zone. Since the apparatus used in this work, was equipped only with conductivity detectors, a different approach for micelle/monomer confirmation was used. As Ogino et al. have shown [22], the length of micelle zone increases with increasing concentration of surfactants and the zone length of free monomers becomes constant at the surfactants concentrations above their CMCs. Fig. 1 demonstrates this effect at various concentrations of CTMA. Unfortunately, due to the occurrence of surfactant

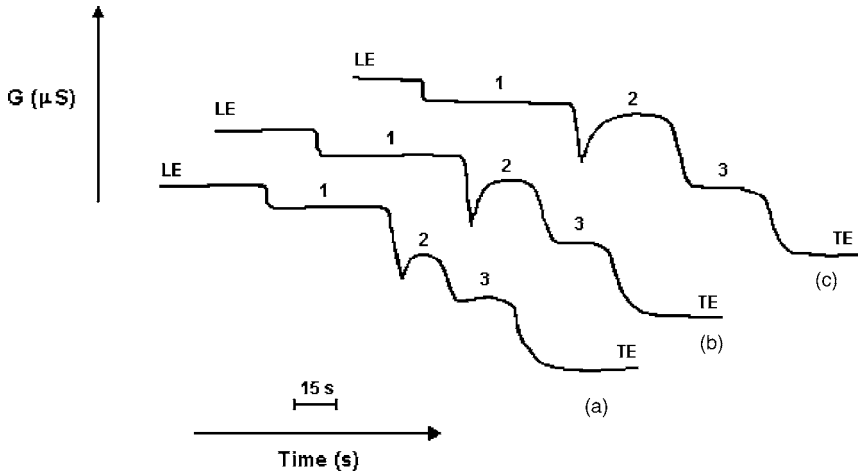

Fig. 1. Isotachopherograms of CTMA in the presence of HEC (0.1%). (a) 0.2 mM, (b) 0.3 mM, (c) 0.4 mM. 1-sodium, 2-micelle, 3-monomer, LE-leading ion, TE-terminating ion.

adsorption, reproducibility of the zone length measurements was very low in order to provide a convincing identification of both zones. Besides, other effects, such as interactions between HEC and surfactant monomers and micelles, e.g. [23], can occur and make the separation very complex. Therefore, HEC was replaced by ethanol in the following experiments.

At 5% (v/v) of ethanol no surfactant zones were registered, probably, because of the CTMA retention in the separation system. Fig. 2 displays the isotachopherograms from 10 to 25% of ethanol when two zones appeared as in the separations with HEC. Their identification was carried out in the same manner as described above, but with better precision

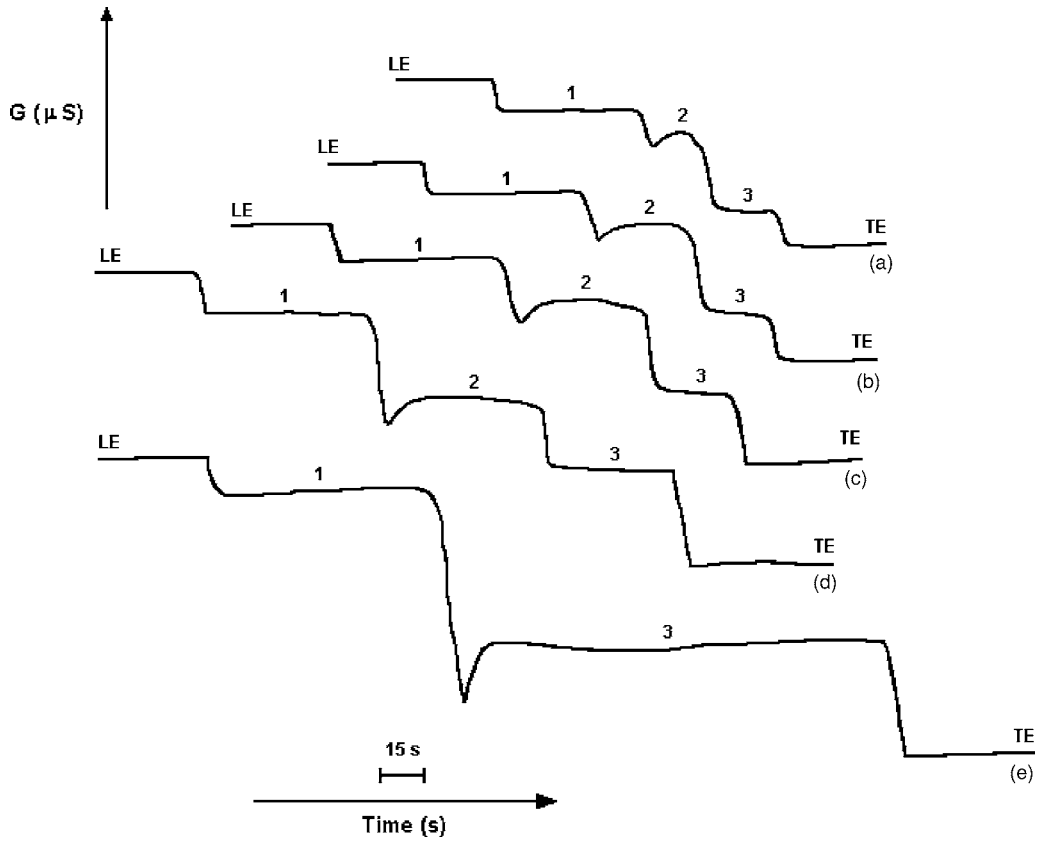

Fig. 2. Isotachopherograms of CTMA (0.25 mM) in the presence of ethanol; (a) 10%, (b) 15%, (c) 20%, (d) 25%, (e) 30%. Zone identifications as in Fig. 1 (the amount of ethanol in the termination electrolyte was fixed at 30%).

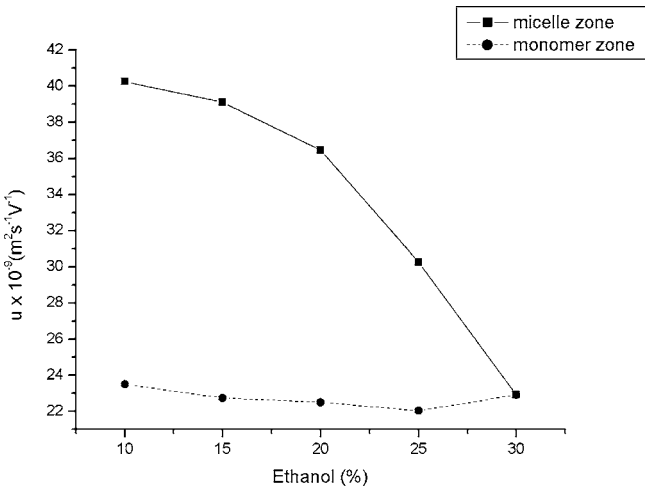

Fig. 3. Dependence of the surfactants mobility u on the concentrations of ethanol. Each point was calculated from two measurements.

providing a reliable zone assignment. It was not surprising that at 30% of ethanol a single zone of the surfactant monomer was found because this alcohol is commonly known to increase the CMCs, e.g. [24]. The length of this zone was prolonging linearly up to 0.25 mM of the CTMA and then a micelle zone appeared in the system again.

Moreover, the electrophoretic mobilities u_x of CTMA monomers and micelles were estimated from these ITP experiments utilising the modified version of Boček et al.'s relationship [25]:

$$u_x = \frac{u_L}{1 + \mathrm{RSH}((u_L/u_S) - 1)} \quad (1)$$

where u_L and u_S are mobilities of the leading (potassium, $u_K = 76.2 \times 10^{-9}\ m^2\ s^{-1}\ V^{-1}$) and the standard (sodium, $u_{Na} = 51.9 \times 10^{-9}\ m^2\ s^{-1}\ V^{-1}$) ions, respectively. The relative step heights (RSH) were used for the definition of zones according to the equation $\mathrm{RSH} = (h_x - h_L)/(h_S - h_L)$, where h_x, h_L, and h_S are the zone heights of the individual surfactant forms, the leading ion and the standard, respectively. (The micelle zone heights were measured on the top of conductivity signals.) The mobility dependence of both CTMA states on the content of ethanol is shown in Fig. 3.

The monomer mobilities were found to be normally distributed within the whole range of ethanol concentrations and they were characterized by the mean value of $(22.8 \pm 0.4) \times 10^{-9}\ m^2\ s^{-1}\ V^{-1}$ ($n = 10$) which is close to that used for the mathematical simulations in this Section. On the contrary, the micelle mobilities were significantly decreasing, likely, as a result of their dissociation and consequential reduction of their charge. At 10% of ethanol in the leading electrolyte the micelle mobility was evaluated at about $40.2 \times 10^{-9}\ m^2\ s^{-1}\ V^{-1}$ which well corresponds with that of tagged micelles ($41.8 \times 10^{-9}\ m^2\ s^{-1}\ V^{-1}$) reported in the paper [15] (compare also with $39.4 \times 10^{-9}\ m^2\ s^{-1}\ V^{-1}$ of dodecyltrimethylammonium hydroxide micelles [26]).

It can be concluded that the estimated mobilities are in consistency with the literal data and thus they confirm the presence of monomers and micelles during the ITP separations in the ethanolic electrolytes. They also indicate that ITP is possible for the study of micellization processes. From the standpoint of the surfactant determination in various samples, it is desirable to entirely suppress the micelle formation. That is why the electrolytes, containing 30% of ethanol, were applied for the next analysis of CTMA in real samples.

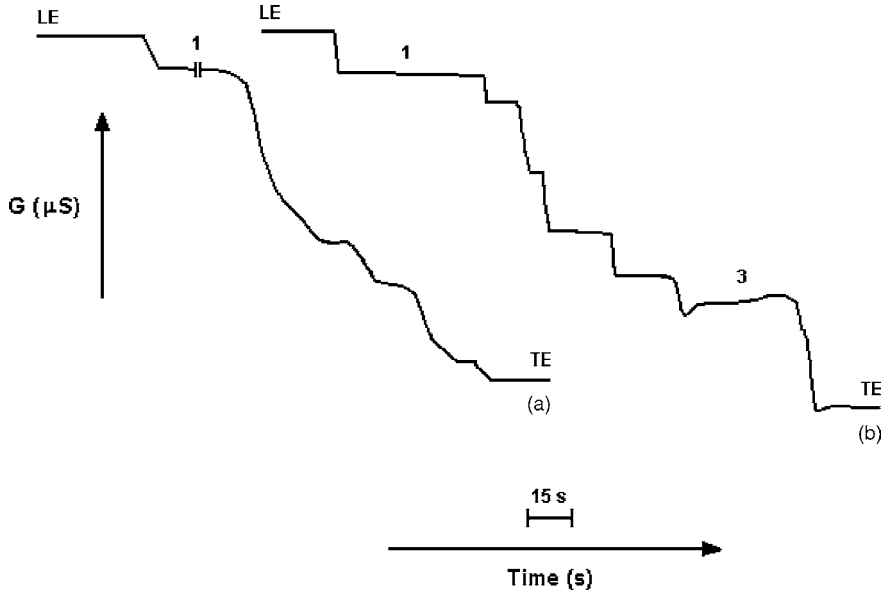

Fig. 4. ITP analysis of a hair conditioner solution. (a) pre-separation capillary, (b) analytical capillary. Zone identifications as in Fig. 1.

3.3. Analyses of CTMA in hair conditioners

The CTMA analyses were carried out via the column-coupling system. Both capillaries were filled with the same leading electrolyte. When aqueous solutions were injected into the pre-separation capillary, the ITP zones moved down also due to the hydrodynamical flow owing to the difference between the densities of samples and the leading electrolyte. To avoid this problem, the leading electrolyte was "thickened" by HEC to obtain 0.2% solution with respect to the density relation: ρ(LE) > ρ(sample) > ρ(TE). The aqueous solutions of CTMA were used for calibration and other testing. The samples were prepared by the dissolution of about 2 g of conditioners in 100 ml of ethanol. Afterwards, a portion of 30 ml was pipetted into 100 ml volumetric flasks, filled up with water and injected into the ITP analyser. The capillaries were rinsed by ethanol after each ITP run.

A typical isotachopherogram of a hair conditioner solution is displayed in Fig. 4. The surfactant zone was well separated from other sample zones and it was identified by the standard addition method. The regression equation of calibration lines was, for instance, $y = (3.22 \pm 0.34)\ x + (-0.02 \pm 0.03)$, $r = 0.9972$ ($n = 7$), where y is time (min) and x is the concentration (mM). The intra-day reproducibility was found at R.S.D. = 3.1% ($n = 5$) and 3.3% ($n = 5$) for a 0.1 mM model solution and a 0.2 mM sample solution, respectively. The detection limits of about 0.02 mM were calculated from the standard deviation of a blank by linear extrapolation of calibration data. One analysis takes about 15 min. On the basis of the obtained results, capillary isotachophoresis seems to be a useful technique for the determination of cationic surfactants in various formulations.

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