ELSEVIER

Journal of Chromatography A, 745 (1996) 281–292

JOURNAL OF CHROMATOGRAPHY A

Separation of ionic and neutral surfactants by capillary electrophoresis and high-performance liquid chromatography

Katja Heinig, Carla Vogt, Gerhard Werner*

University of Leipzig, Department of Chemistry, Linnèstrasse 3, 04103 Leipzig, Germany

Abstract

Some of the most important anionic, cationic and non-ionic surfactants can be separated by CE; HPLC was used as a reference. A comparison of both methods with respect to separation efficiency, reproducibility and detection limits is presented. Linear alkylbenzenesulfonates were analyzed in river water, sewage sludge and laundry detergents. Chromatographic separations on RP-8 columns led to a resolution of alkyl homologues. In CE, determination of the sum was performed in a pure aqueous buffer. Using electrolytes containing acetonitrile, homologous separation could be obtained. The addition of α-cyclodextrin allowed the separation of isomers. Aliphatic anionics (alkylsulfonates and -sulfates) could be determined by HPLC with conductivity detection and CE with indirect UV detection. Various chromophores like salicylate or dodecylbenzenesulfonate and organic modifiers were compared. Sodium dodecyl sulfate could be analyzed in toothpaste. Important representatives of cationics (quaternary alkyl and benzalkyl ammonium compounds, pyridinium salts) were separated using direct and indirect UV detection. For electrophoretic separation, high content of organic solvents was necessary to obtain a sufficient peak resolution. The results of method development were applied to the analysis of cetylpyridinium chloride in mouth-wash. Non-ionic surfactants of the polyoxyethylene type are separated into ethoxylate homologues by HPLC on aminosilica columns. CE separation was carried out in electrolytes containing high content of acetonitrile and SDS and is based on the formation of association complexes between the non-ionic analytes and anionic surfactants. Chromatograms and electropherograms may be considered as fingerprints of the substance for product control and to determine the average number of ethylene oxide units of unknown products.

Keywords: Surfactants; Alkylbenzenesulfonates, linear; Polyethoxylates; Cetylpyridinium chloride

1. Introduction

Surfactants possess both hydrophilic and hydrophobic characteristics, due to the polar head group and the long-chain alkyl group of the molecule. Considering the charge of the hydrophilic group, surfactants can be divided into anionic, cationic, amphoteric and non-ionic compounds. Their ability to decrease the surface tension and to form micelles is the reason for the widespread use of surfactants especially in detergent industry [1]. After usage, the surfactants enter surface waters by passing sewage treatment facilities. They can cause a disturbance of the ecological equilibrium, due to toxic impacts on aquatic organisms [2]. Therefore, the determination of surfactants is important not only for product control but also in environmental analysis.

The German standard methods specify so-called "collective" techniques which provide total contents of surfactant classes [3]. These methods are not selective, because they suffer from many interfering substances and do not give any information about the individual homologues. Therefore, specific determi-

*Corresponding author.

0021-9673/96/$15.00
PII S0021-9673(96)00399-8

nation techniques became more important. For the identification of surfactants, IR [4], UV–Vis [5] NMR [6] and MS [7] are preferred. Potentiometry with ion-selective electrodes [8] is used for quantification. Chromatographic techniques like TLC [9], GC [10], SFC [11], electrophoresis [12] and HPLC are efficient separation methods for the analysis of complex surfactant mixtures. The potential of CE has been increasingly applied for surfactant separations.

Anionic surfactants are applied mainly for laundry detergents, cleaning agents, cosmetics and hygienic products. Linear alkylbenzenesulfonates (LAS) are the most important anionics. They are present in commercial formulations as complex mixtures of C_{10}–C_{14} homologues and of positional isomers resulting from the attachment of the phenyl ring to the carbon atoms (from the second to the central one) of the linear alkyl chain.

High-performance liquid chromatography (HPLC) is currently the most suitable method for the determination of LAS. Ion-exchange HPLC is useful in identifying surfactant classes but inefficient in separating individual homologues [13]. Reversed-phase HPLC permits the resolution of homologues and isomers, depending on chromatographic conditions. With the use of C_{18} columns the separation of LAS isomers was possible [14–17]. The analysis of LAS using C_8 columns leads to the separation of homologues [18–21]. Nevertheless, identification and determination of surfactants in environmental samples are often difficult, because the concentration is low and the matrix is very complex. Therefore, sample preconcentration and purification are necessary, usually carried out by solid-phase extraction (SPE) [22,23] or gaseous stripping into ethyl acetate [24].

Alkylsulfonates and -sulfates are mostly removed by biological degradation and therefore not so important in environmental analysis. Nevertheless, the development of analytical methods is of interest for product control. Aliphatic anionic surfactants have been separated by ion-pair chromatography with indirect UV detection using absorbing co-ions [25–27] or counter-ions [28]. Separations on anion-exchange columns were performed [29]. Using post-column derivatization, anionic surfactants are transformed into fluorescent substances detectable with high sensitivity [30]. An alternative detection mode is conductivity with electrical or chemical suppression of the background signal [31,32].

Most investigations of surfactant analysis in CE were started in the field of anionics. Linear alkylbenzenesulfonates have been analyzed using borate or phosphate buffers at pH 7–9, with acetonitrile as organic modifier [33]. Desbene et al. compared CZE with MEKC separations of LAS with chain length of C_2–C_{12} [34]. Separations of alkylbenzenes and its sulfonates were carried out in buffers with high organic contents [35]. Determination of LAS in river water [36] and isomeric separations with cyclodextrins were performed [37]. Alkylsulfonates have been separated using indirect UV detection in benzoate and naphthalenesulfonate electrolytes [38]. The addition of Mg^{2+} leads to a better peak resolution of various anionics [39]. Sodium dodecyl sulfate was determined in water using benzoate as absorbing buffer [40]. Furthermore, naphthalenemono-, di- and trisulfonates have been applied as chromophores [41].

Cationic surfactants are used in a variety of industrial and consumer applications, e.g. disinfectants, antistatic agents, foam depressants, cosmetics, and textile softeners.

By far the most promising and convenient method for industrial and environmental analysis of cationics has been HPLC. Quaternary ammonium compounds were separated commonly by ion-pair chromatography with non-polar stationary phases and Cl^- and ClO_4^- as counter ion [32,42]. Direct UV and suppressed conductivity detection were used. For indirect UV detection of non-absorbing compounds, chromophoric eluents were applied [26,43]. The application of ion-exchange columns has been reported [44]. Several authors separated cationic surfactants on a cyan-amino-bonded silica column with a non-aqueous mobile phase and direct conductivity detection [45,46].

The analysis of cationic surfactants by CE is problematical because of the strong adsorption of these substances at the inner surface of the fused-silica capillary. Nevertheless, the addition of organic modifiers in large amounts helps to overcome this problem. Quaternary alkyl and benzalkyl ammonium compounds are separated using 50% THF as organic modifier [47]. For indirect detection, benzalkyltrimethylammonium chlorides were used as

absorbing buffer components. For the separation of surfactant herbicides like paraquat, alkaline salts were used to reduce wall adsorption [48].

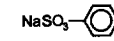
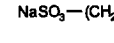
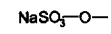
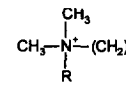
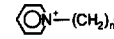
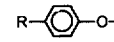
Polyoxyethylene-based nonionic surfactants have a statistic homologous distribution of ethylene oxide units. Alcohol ethoxylates (AEO), the most important nonionic surfactants, are two-dimensional homologous mixtures: both length of alkyl chain and number of ethylene oxide units are varying. AEO are used commercially in laundry detergents, cleaning agents, cosmetics, herbicides. Alkylphenol polyethoxylates (APEO) are applied in octyl- and nonylphenol types (OPEO, NPEO). The application of APEO in laundry detergents was restricted because of insufficient biological elimination with toxic metabolites [2]. They are used in the flotation of ore minerals, mineral oil hauling and as auxiliary substances in textile industry, dye and varnish production.

Performing HPLC on non-polar columns, nonionic surfactants are separated according to alkyl chain length [49–51]. A wide variety of polar stationary phases is applied for the separation of ethylene oxide homologues [52–58]. Alcohol polyethoxylates have been derivatized before analysis by reacting with 3,5-dinitrobenzoylchloride or phenylisocyanate [51,59].

Non-ionics are only infrequently investigated by capillary electrophoresis [60]. The electrophoretic separation of neutral molecules requires the application of an ionic additive to form a pseudophase. Sodium dodecyl sulfate (SDS) is commonly used in micellar electrokinetic capillary chromatography (MECC). Hydrophobic analytes are difficult to resolve in MECC owing to their low solubility in water and high partition coefficients into the micellar phase. With the addition of organic modifiers in concentrations higher than 20%, analytes are solubilized and the micelle formation will be inhibited. The interaction between nonionic analytes and surfactants is called solvophobic association [61]. Separation is based on differences in the strength of analyte–surfactant association complexes, which results in differences in effective electrophoretic mobilities. This mode of CE is useful to separate mixtures of nonionic surfactant homologues containing a hydrophobic alkyl chain.

In this paper, the authors report on the separation of some representatives of anionic, cationic and nonionic surfactants (Table 1) by CE and HPLC. The influence of the separation conditions is discussed; a comparison of CE and HPLC is presented. Environmental and household samples are analyzed.

Table 1
Investigated compounds

Linear alkylbenzenesulfonates	 R=C_nH_{2n+1}, n=10-13
Alkylsulfonates	
Alkylsulfates	
Quaternary alkylammonium salts	 R=CH_3, C_6H_5
Alkylpyridinium salts	
Alkylphenol polyethoxylates	 R=C_8H_{17}, C_9H_{19}, n=2-100

2. Experimental

2.1. Apparatus

2.1.1. High-performance liquid chromatography

For the separation of surfactants with UV detection a Beckman (Palo Alto, USA) System Gold consisting of a 126 programmable solvent module, an injection valve with 20 μl loop and a 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 (Vienna, Austria). The detector was set at 225 nm (LAS), 214 nm (cationic surfactants) and 277 nm (non-ionics). Separations of ionic surfactants were performed on a C_8 column, 250×4,6 mm (Beckman). Nonionics are separated using a NH_2 column 250×4 mm, (Macherey-Nagel, Düren, Germany). Elution was carried out in isocratic or gradient mode with a flow-rate of 1 ml/min. Separation of aliphatic anionics using conductivity

detection was performed on a Bischoff IonChem 2000 (Leonberg, Germany). Prior to use the prepared eluents were degassed in an ultrasonic bath for 5 min under vacuum.

2.1.2. Capillary electrophoresis

CE was performed on P/ACE 2050 and 5510 systems (Beckman), monitored by an IBM PC using Gold software (Beckman). The UV detector was set at 200 nm for direct and 214 nm for indirect detection. Injections (at the anodic end) were performed in the pressure mode and the injection time was set at 5 or 10 s. Fused-silica capillaries of 57 cm length (50 cm to the detection window)×75 μm I.D. were used (CS Chromatographie Service, Langerwehe, Germany). Operation voltage was 20 kV.

2.2. Chemicals

All substances used were of analytical grade, organic solvents of HPLC grade. Na_2HPO_4, NaH_2PO_4, $Na_2B_4O_7$, H_3BO_3, HCl, $NaClO_4$, acetic acid and sodium acetate were from Laborchemie Apolda (Germany). Organic solvents for CE (methanol, acetonitrile, ethanol, propanol, 2-propanol, tetrahydrofuran) were obtained from Merck (Darmstadt, Germany). Methanol, acetonitrile, 2-propanol and *n*-hexane for HPLC were from Roth (Karlsruhe, Germany). UV active buffer substances for CE with indirect detection were obtained from Merck. Sodium dodecyl sulfate was supplied by Merck, other sulfates and sulfonates by Sigma (Deisenhofen, Germany). Cyclodextrins were used as received from Fluka (Neu-Ulm, Germany). Buffer solutions and mobile phases were prepared using triply distilled water.

2.2.1. Anionics

Marlon A-390, a commercial LAS product, was supplied by Chemische Werke Hüls (Marl, Germany). It is a surfactant mixture containing C_{10}–C_{13} homologues and four to six phenyl isomers per homologue. Pure isomeric standards are also obtained from Hüls. The household detergent "Spee gekörnt" was produced by Waschmittelwerke Genthin (Germany) and "Spee" was from Henkel, Düsseldorf/Genthin (Germany). Water samples from German rivers were preserved with HNO_3 to prevent further microbial degradation and stored at 4°C. Filtration was carried out to remove solids. 1000 ml of each water sample were prepared by SPE according to [33]. Extraction cartridges (RP 18, 400 mg and SAX, 500 mg) were obtained from Bakerbond (Phillipsburg, USA). Sewage sludge was investigated by extracting 2 g with 100 ml methanol and NaOH at 70°C for 2 h.

Table 2
Composition of nonionic surfactant mixtures

	Alkyl chain length	Average ethyleneoxide units
Igepal CA-720	8	12
Triton CF 10	8	?
Präwozell N 5,5	9	5,5
Präwozell N12	9	12
Präwozell N 20	9	20
Präwozell N 30	9	30
Präwozell N 55	9	55

Alkylsulfonate standards were obtained from Sigma; TEEPOL HB 7, a mixture of secundary alkyl sulfates, was from Aldrich (Steinheim, Germany). The toothpaste "Mentadent intensive" (Elida Gibbs, Hamburg, Germany) was analyzed.

2.2.2. Cationics

Cetylpyridinium chloride, alkyl benzyl dimethylammonium chloride ("Benzalkoniumchlorid") and dodecyl-, tetradecyl-, hexadecyl- and octadecyltrimethylammonium bromides were obtained from Sigma. The mouth-wash "Odol med Zahnfleisch aktiv" (Lingner and Fischer, Germany) was analyzed without any preparation.

2.2.3. Nonionics

The compositions of the surfactants mixtures used are shown in Table 2. Igepal CA-720 was supplied by Aldrich. The APEO Präwozell N5,5, N12, N20, N30 and N55 were of technical grade from BUNA AG (Schkopau, Germany). Triton CF 10 was obtained from Fluka.

3. Results and discussion

3.1. Anionic surfactants

3.1.1. Linear alkylbenzenesulfonates

In former investigations LAS have been analyzed using HPLC and CE [37]; a comparison of both methods was presented. With HPLC on RP columns with lower chains a separation of homologues is easily possible; on C_{18} columns an isomer separation within groups of the same chain is achieved. Performing CE in aqueous buffers, the sum of LAS can be determined. In buffers containing >20% acetonitrile a separation of homologues takes place, above 30% acetonitrile the well separated 2-C isomer can be detected. With the addition of α-cyclodextrin a complete separation of isomers is possible.

In the following, applications of the developed methods for the separation of LAS are presented. The quantification is based on external calibration using the technical product Marlon A-390 containing 89.5% LAS.

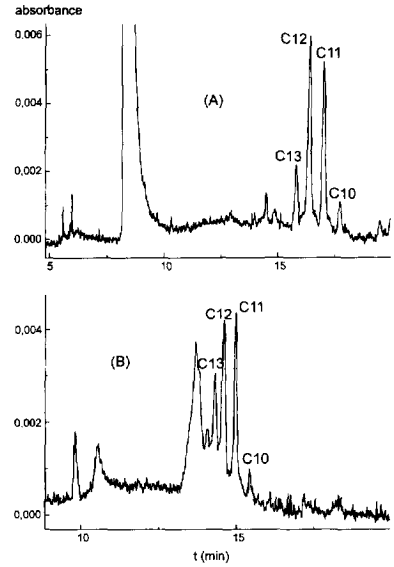


Fig. 1. Determination of LAS in environmental samples by CE: (A) river Elbe, (B) sewage sludge, buffer: 100 m*M* phosphate pH 6.8, 30% (v/v) acetonitrile.

Determination of the sum

The laundry detergents "Spee gekörnt" produced in 1985 and "Spee" manufactured in 1994 have been compared with respect to LAS content: the former produced product contains 24.8%, the new detergent only 16.9% where a part of LAS has been replaced by nonionic surfactants.

Homologous separation

HPLC and CE were used for the analysis of environmental samples. LAS homologues in river water were separated after 1000-fold preconcentration and a sewage sludge was analyzed after methanolic extraction. The electrophoretic separations are presented in Fig. 1, the results of quantification are listed in Table 3. The differences between the surfactant contents determined by HPLC and CE can be explained by the higher RSD of CE, the lower detection limit and the overlapping of LAS peaks with disturbing components in case of the sludge sample.

Isomeric separation

LAS separation into constitutional isomers was performed using α-CD. It was assumed, that only the alkyl chain is included into the hydrophobic cyclodextrin cavity. To establish theoretical foundations, pure isomers were investigated. Separating a homologous mixture of 2-C isomers (Fig. 2A), the compounds with longer alkyl chains migrate faster to the detection end due to lower electrophoretic mobility toward the anode. Furthermore, the hydrophobic interactions of the relatively non-polar long chains with the CD phase are stronger than that of the shorter homologues. In Fig. 2B the separation of an isomeric mixture of the C11 homologue is presented. The more the phenyl ring position changes from the end to the center of alkyl chain, the longer the migration time of the isomer towards the detector. The 6-C isomer reaches the detector at last because of lower interaction with CD, due to the shorter alkyl chain (twice six carbon atoms at the phenyl bonded C) and therefore lower hydrophobicity. Another fact is the handicapped inclusion by sterical effects.

The pure isomers are used for the peak identification in Marlon A-390. Fig. 3 shows the electropherogram. Because of the overlapping of homologous series no identification from theoretical

Table 3
Determination of LAS in environmental samples

		HPLC		CE
River water (Elbe)	117.3 μg/l:	6.7% C_{10}	103 μg/l:	6.2% C_{10}
		35.8% C_{11}		39.9% C_{11}
		43.6% C_{12}		43.8% C_{12}
		13.9% C_{13}		10.1% C_{13}
Sewage sludge	2.39 mg/g:	4.6% C_{10}	2.27 mg/g:	4.4% C_{10}
		27.8% C_{11}		32.9% C_{11}
		43.3% C_{12}		40.4% C_{12}
		24.3% C_{13}		22.3% C_{13}

HPLC: 0.1 *M* $NaClO_4$–methanol (20:80), CE: conditions are described in Fig. 1.

considerations was possible. Table 4 presents the peak assignment from addition of the isomer standards to the product. The 4-C_{12}, 6-C_{12}, 5-C_{13} and 7-C_{13} isomers are not available; therefore identification could only be supposed.

3.1.2. Aliphatic anionics

To analyze the non-absorbing alkylsulfonates and -sulfates by HPLC, conductivity detection was carried out using a mobile phase providing a low basic signal. In CE, indirect UV detection was performed using absorbing organic buffers. Fig. 4A presents the

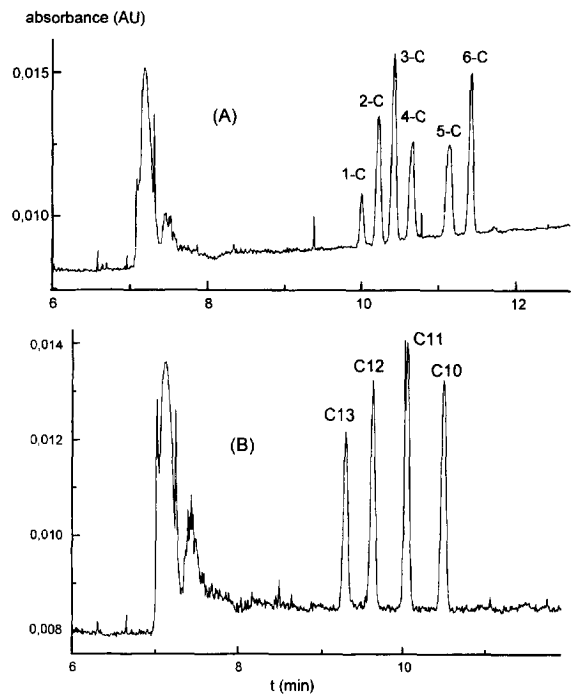


Fig. 2. Separation of pure LAS isomers using α-cyclodextrin: (A) separation of all isomers of the C_{11} homologue, (B) homologous separation of 2-C isomers, buffer: 100 m*M* phosphate pH 6.8, 15 m*M* α-CD, 20% (v/v) acetonitrile.

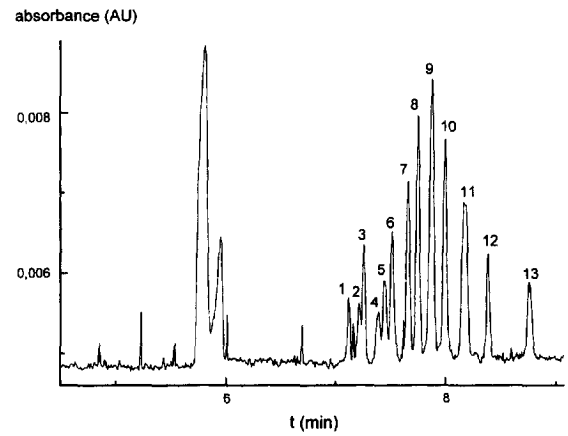


Fig. 3. Isomeric separation of 0.12 g/l Marlon A-390, conditions as in Fig. 2.

Table 4
Identification of isomers in Marlon A-390

Peak number	Isomers (identified)	Isomers (supposed)
1	2-C_{13}	
2	3-C_{13}	
3	2-C_{12}	
4	4-C_{13}	
5	3-C_{12}	5-C_{13}
6	2-C_{11}	5-C_{13}/4-C_{12}
7		5-C_{13}/4-C_{12}
8	3-C_{11}/6-C13	4-C_{12}
9	4-C_{11}/2-C_{10}/5-C_{12}	7-C_{13}
10	3-C_{10}	6-C_{12}/7-C_{13}
11	5-C_{11}/4-C_{10}	6-C_{12}/7-C_{13}
12	6-C_{11}	
13	5-C_{10}	

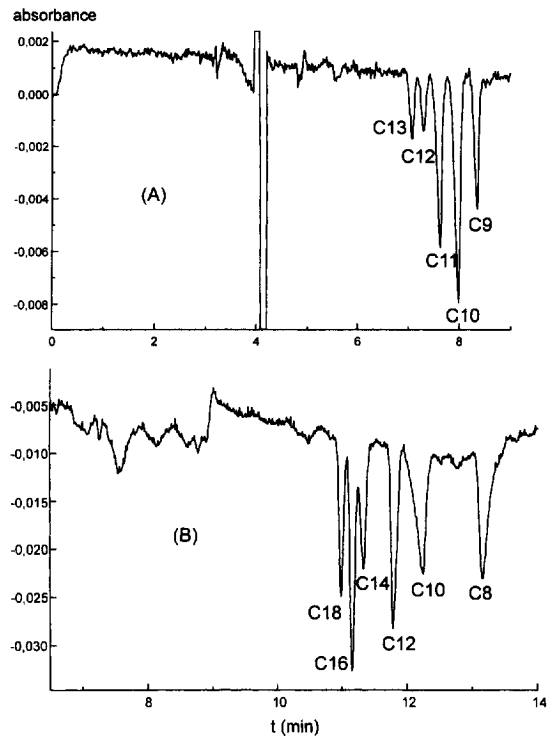


Fig. 4. Separation of aliphatic anionics by CE: (A) 2 g/l TEEPOL HB 7 (alkylsulfates), buffer: 20 m*M* salicylate pH 6, 30% acetonitrile, (B) alkylsulfonates, sample size: 1 m*M* each, buffer: 5 m*M* dodecylbenzenesulfonate, 5 m*M* phosphate pH 6.8, 30% acetonitrile.

separation of TEEPOL HB 7, a mixture of alkyl sulfates, in a salicylate buffer. Electrophoretic behavior is affected by nature and concentration of the electrolyte and the content of organic modifier which was used to achieve baseline resolution. Table 5 shows the influence of various electrolytes and organic modifiers on peak resolution and migration time.

To improve peak shape in indirect detection, chromophores possessing a similar electrophoretic mobility as the analytes have to be used. Technical linear alkylbenzenesulfonate was supposed to comply with this condition; it was applied for the separation of alkylsulfonates presented in Fig. 4B.

To compare HPLC with CE, the analysis of sodium dodecylsulfate in toothpaste was performed (Fig. 5); quantitative results are listed in Table 6.

3.2. Cationics

The HPLC separations were carried out by ion-pair chromatography using Cl^- as counter ion. In CE, cationic surfactants were separated in buffers containing high contents of organic modifier to prevent adsorption of the analytes at the inner capillary surface. THF was found to provide the best peak resolution in acceptable analysis time. Fig. 6A

Table 5
(A) Influence of increasing acetonitrile content in various buffers (each 5 m*M*, pH 6) on peak resolution R_s of alkyl sulfates and (B) Influence of increasing content of various organic modifiers in a 5 m*M* salicylate eleactrolyte (pH 6) on peak resolution R_s of alkyl sulfates

(A) Acetonitrile (%)	R_s			
	Salicylate	*p*-Hydroxybenzoate	Phthalate	Benzoate
0	0.23	0.73	0.60	0.39
10	0.39	1.01	0.63	0.54
20	0.63	1.07	0.79	0.65
30	0.80	1.38	0.97	0.73
40	0.89	1.68	1.34	1.11
(B) Organic content (%)	R_s			
	Methanol	Ethanol	Propanol	2-Propanol
0	0.23	0.23	0.23	0.23
10	0.61	0.38	0.49	0.60
20	0.81	0.90	0.62	0.95
30	0.83	1.17	1.14	1.37
40	1.00	2.62	–	1.40

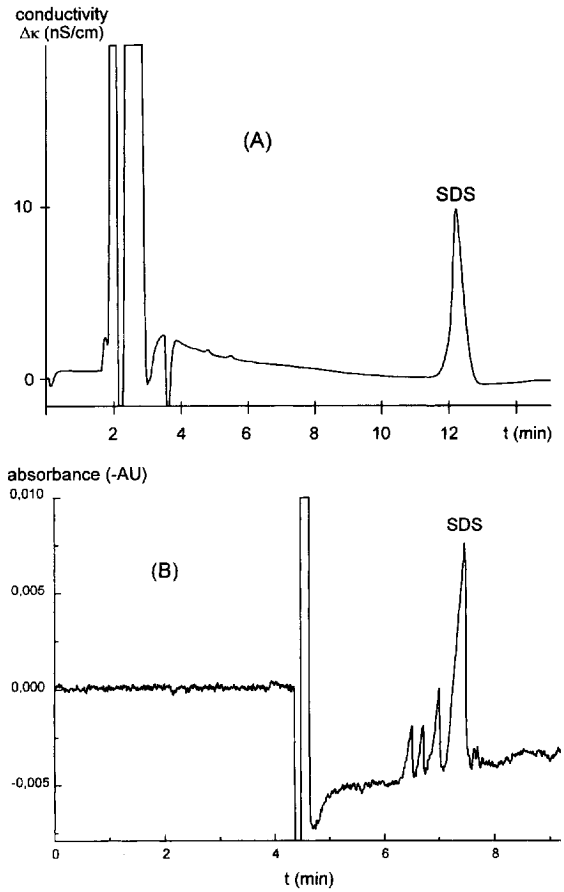


Fig. 5. Determination of SDS in toothpaste: (A) HPLC, eluent: 1 m*M* sodium acetate–methanol (30:70), (B) CE, conditions as in Fig. 4B.

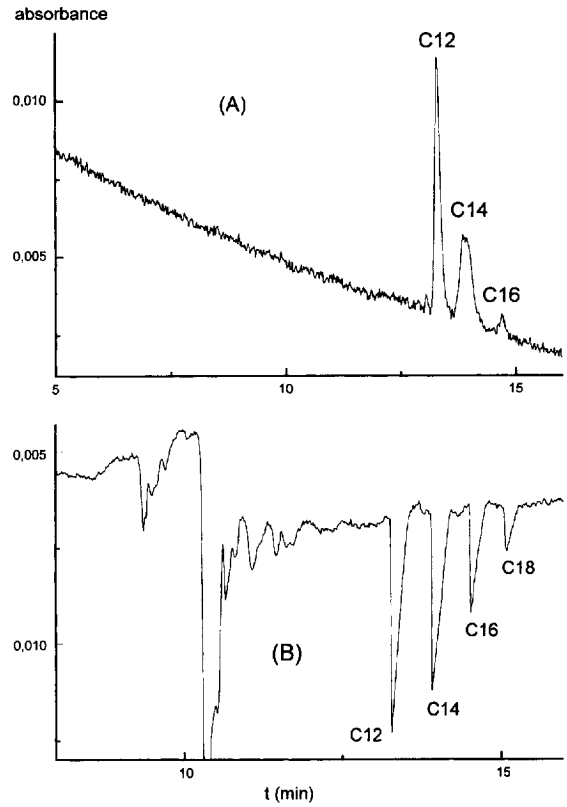


Fig. 6. Separation of cationic surfactants using CE: (A) 0.2 g/l benzalkonium chloride, buffer: 50 m*M* phosphate pH 6.8, 55% (v/v) THF, (B) each 1 m*M* alkyltrimethylammonium bromides, buffer: 50 m*M* phosphate pH 6.8, 5 m*M* benzyltrimethylammonium chloride, 3 m*M* SDS, 50% (v/v) THF.

shows the separation of benzalkyl compounds (benzalkonium chloride).

For the determination of substances without chromophores an absorbing buffer component is necessary to carry out CE with indirect detection. Best separations could be obtained using benzyltrimethylammonium chloride. Because of the differences in electrophoretic mobilities of the slow moving surfactants and the faster moving absorbing buffer component a peak tailing resulted. The addition of SDS leads to an improvement of peak resolution due to the formation of ion pairs. Alkyltrimethylammonium compounds have been separated (Fig. 6B).

HPLC and CE were compared with respect to separation efficiency, reproducibility (in terms of RSD) and limit of detection (LOD) using the analysis of cetylpyridinium chloride (CPC) in mouth-wash (Table 7); the separations are presented in Fig. 7. Acetonitrile was used as buffer additive in CE to obtain as well a sufficient resolution of CPC from other sample components as a short analysis time.

Table 6
Comparison of HPLC and CE using the determination of SDS in toothpaste

	HPLC	CE
Results of quantification (mg/l)	7.78	7.69
Correlation coefficient	0.9988	0.9980
Reproducibility in terms of RSD (%)	0.53	9.65
Limit of detection (mg/l)	$4.6 \cdot 10^{-6}$	$8.4 \cdot 10^{-5}$

Conditions are described in Fig. 5.

Table 7
Comparison of HPLC and CE using the determination of CPC in mouth wash

	HPLC	CE
Results of quantification (mg/l)	337.9	326.4
Correlation coefficient	0.9994	0.999
Reproducibility in terms of RSD (%)	3.54	6.12
Limit of detection (mg/l)	$7 \cdot 10^{-5}$	$7.3 \cdot 10^{-4}$

Conditions are described in Fig. 7.

3.3. Non-ionics

In HPLC separations of APEO "Präwozell N" were performed with regard to ethylene oxide homologues (Fig. 8). Substances are eluted in order of increasing number of EO groups because of increasing interaction with the polar stationary phase.

Fig. 9 shows the CE analysis of these compounds using SDS to provide a charged pseudophase and high contents of organic solvent (acetonitrile), which

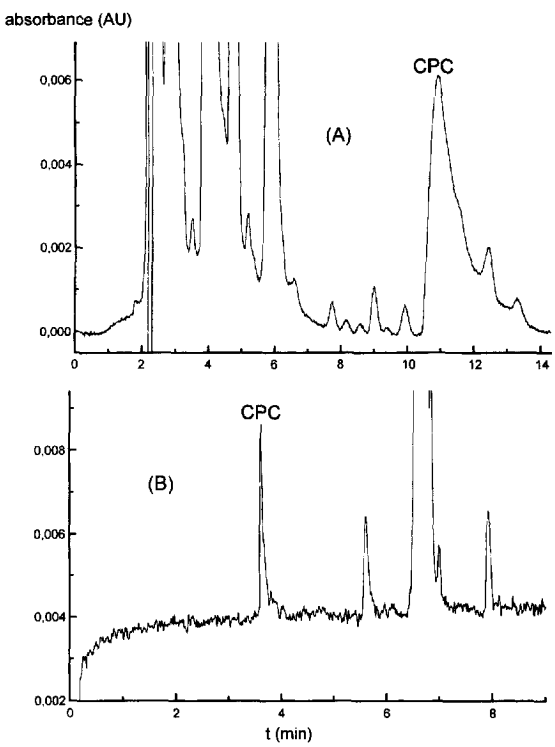


Fig. 7. Determination of CPC in mouth wash: (A) HPLC, eluent: 0.02 *M* HCl–acetonitrile (50:50) in 15 min to 20:80, (B) CE, buffer: 50 m*M* phosphate pH 6.8, 50% acetonitrile.

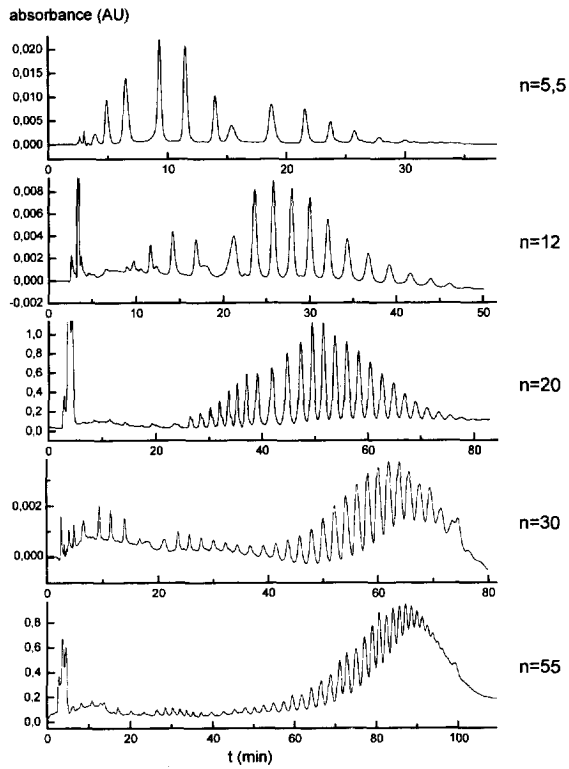


Fig. 8. HPLC separation of nonylphenol polyethoxylates ('Präwozell'), eluent: *n*-hexane–2-propanol (9:1) in 100 min to 2-propanol–water (9:1).

is known to inhibit micelle formation in concentrations higher than 20%. Ethylene oxide homologues partition between organic and SDS phase in dependence on hydrophobicity. The homologues with less EO groups interact stronger with SDS than the more polar highly ethoxylated compounds. Therefore, migration order in CE is reversed compared to elution order in HPLC: nonionics are detected in order of decreasing number of EO groups. The content of acetonitrile necessary to achieve a homologous separation depends on the average EO number. For a sufficient peak resolution of the EO 12 a higher organic content has to be applied than for the separation of EO 55.

CE determination of APEO can be used for product control due to the dependence of migration time on average number of ethylene oxide units. Furthermore, unknown substances can be identified with respect to alkyl chain length and EO numbers

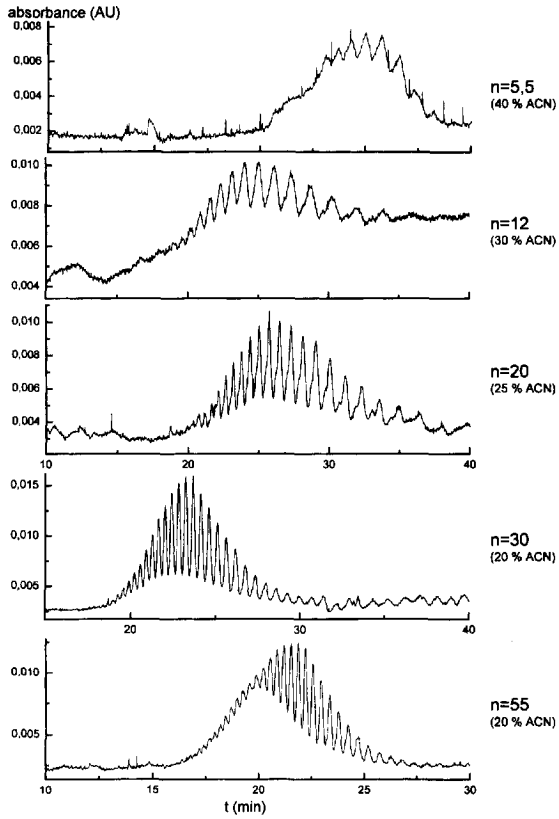


Fig. 9. CE separation of nonylphenol polyethoxylates ('Präwozell'), buffer: 10 m*M* phosphate pH 6.8, 70 m*M* SDS, acetonitrile content see figure.

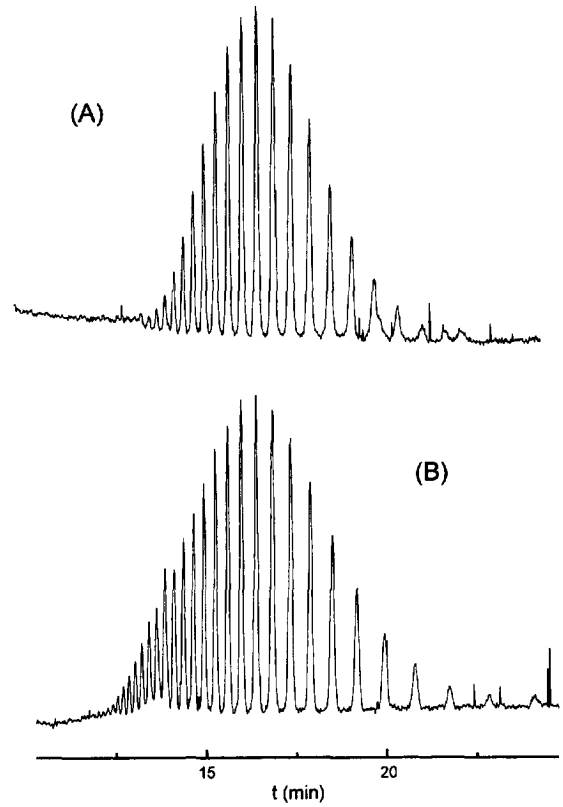


Fig. 10. Comparison of (A) Igepal CA-720 and (B) Triton CF 10 to estimate the ethylene oxide number, buffer: 10 m*M* phosphate pH 6.8, 70 m*M* SDS, 35% acetonitrile.

comparing the peak pattern with known APEO. Fig. 10A shows the electropherogram of Igepal CA-720, an octyl-PEO with 12 EO groups in average; 10B shows the separation of Triton CF 10 (degree of ethoxylation not specified). From the similarity of the electropherograms could be established, that Triton CF contains also 12 EO groups.

Electrophoretic separation of APEO provides sufficient sample information in short analysis time (decision on alkyl chain length and estimation of ethylene oxide number). The main advantage is the possibility to change the buffer composition easily in order to optimize separation conditions. For the analysis of complex mixtures of non-ionics (e.g. in environmental samples) HPLC is to be preferred. A comparison of both methods with regard to quantification is presented in Table 8.

4. Conclusions

CE provides a high-resolution separation of a large number of compounds in a small sample volume. A rapid method development is possible by changing the electrolyte composition easily. These advantages increasingly have been used for surfactant analyses.

Linear alkylbenzenesulfonates could be determined in technical products and laundry detergents as well as in environmental samples. The application of CE to the direct and indirect analysis of anionic and cationic surfactants without sample preparation is possible.

The high efficiency of CE in the separation of ionic surfactants could not be achieved for non-ionics because of the complexity and lack of charge. In this case, chromatographic techniques are superior

Table 8
Comparison of HPLC and CE in analysis of non-ionics

	HPLC	CE
Correlation coefficient	0.9998	0.998
Reproducibility of peak area in terms of RSD (%)	5.16	4.45
Reproducibility of separation time (%)	0.92	1.42
Limit of detection (mg/l)	36.6	100

Conditions are described in Figs. 8,9.

to CE. Another drawback is the higher detection limit compared to HPLC.

Acknowledgments

The authors want to acknowledge the German Environmental Foundation for financial support. We thank Dr. Schleich, Hüls AG for supplying us with isomeric LAS standards and the BUNA AG for providing us with technical non-ionics.

References

[1] G. Kosswig and H. Stache, Die Tenside. Carl Hanser, München, 1993.
[2] K.-G. Malle, Git Fachz. Lab., 5 (1993) 422–429.
[3] Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung, Summarische Wirkungs- und Stoffkenngrößen (Gruppe H).
[4] D.O. Hummel, Git Fachz. Lab., 5 (1994) 439–447.
[5] H. Hellmann, Buch der Umweltanalytik Bd. 2, GIT Verlag, 1991, p. 53.
[6] E.M. Thurmann, T. Willoughby, L.B. Barber and K.A. Thorn, Anal. Chem., 59 (1987) 1798–1802.
[7] H. Hon-Nami and T. Hanya, J. Chromatogr., 161 (1978) 205.
[8] H.-U- Dammer, Tenside Surf. Det., 32 (1995) 12–16.
[9] H.T. Rasmussen, J. High Resolut. Chromatogr., 17 (1994) 593–596.
[10] H. Hellmann, Tenside Surf. Det., 28 (1991) 111–117.
[11] P. Sandra and F. David, J. High Resolut. Chromatogr., 13 (1990) 414.
[12] J.R. Bodenmiller and H.W. Latz, Anal. Chem., 44 (1972) 926–930.
[13] Y. Yokoyama, M. Kondo and H. Sato, J. Chromatogr., 643 (1993) 169–172.
[14] A. Nakae, K. Tsuji and M. Yamanaka, Anal. Chem., 52 (1980) 2275.
[15] E. Mattijs and H. De Henau, Tenside Surf. Det., 24 (1987) 193–198.
[16] L. Comellas, J.L. Portillo and M.T. Vaquero, J. Chromatogr. A, 657 (1993) 25–31.
[17] M.A. Castles, B.L. Moore and S.R. Ward, Anal. Chem., 61 (1989) 2534–2540.
[18] A. Di Corcia, M. Marchetti and R. Samperi, Anal. Chem., 63 (1991) 1179–1182.
[19] A. Markomini, S. Capri and W. Giger, J. Chromatogr., 403 (1987) 243–252.
[20] A. Markomini, A. Di Corcia, R. Samperi and S. Capri, J. Chromatogr., 644 (1993) 59–71.
[21] W.A.A. Senden and R. Riemersma, Tenside Surf. Det., 27 (1990) 46–51.
[22] A. Kreisselmeier, M. Schoester and G. Kloster, Fresenius J. Anal. Chem., 353 (1995) 109–111.
[23] Y. Yokoyama and H. Sato, J. Chromatogr., 555 (1991) 155–162.
[24] R. Wickbold, Tenside Surf. Det., 9 (1972) 173.
[25] J.A. Boiani, Anal. Chem., 59 (1987) 2583–2586.
[26] M. Denkert, L. Hackzell, G. Schill and E. Sjögren, J. Chromatogr., 218 (1981) 31–34.
[27] S.A. Shamsi and N.D. Danielson; Chromatographia, 40 (1995) 237–246.
[28] G. Liebscher, G. Eppert, H. Oberender, H. Berthold and H.G. Hauthal, Tenside Surf. Det., 26 (1989) 195–197.
[29] J.R. Larson, J. Chromatogr., 356 (1986) 379–381.
[30] F. Smedes and J.C. Kraak, J. Chromatogr., 247 (1982) 123–132.
[31] J. Weiss, J. Chromatogr., 353 (1986) 303–307.
[32] N. Pan and D.J. Pietrzyk, J. Chromatogr. A, 706 (1995) 327–337.
[33] J. Zweigenbaum, Chromatogram, 11 (1990) 9–10.
[34] P.L. Desbene, C. Rony, B. Desmazieres and J.C. Jaquier, J. Chromatogr., 608 (1992) 375–383.
[35] P.L. Desbene and C.M. Rony, J. Chromatogr. A, 689 (1995) 107–121.
[36] K.D. Altria, I. Gill, J.S. Howells, C.N. Luscombe and R.Z. Williams, Chromatographia, 40 (1995) 527–531.
[37] C. Vogt, K. Heinig, B. Langer, J. Mattusch and G. Werner, Fresenius J. Anal. Chem., 352 (1995) 508–514.
[38] J. Romano, P. Jandik, W.R. Jones and P.E. Jackson, J. Chromatogr., 546 (1991) 411–421.
[39] S. Chen and D.J. Pietrzyk, J. Chromatogr. A, 657 (1993) 2770–2775.
[40] J.M. Gibbons and S.H. Hoke, J. High Resolut. Chromatogr., 17 (1994) 665–667.

[41] S.A. Shamsi and N.D. Danielson, Anal. Chem., 66 (1994) 3757–3764.
[42] A. Nakae, K. Kunihiro and G. Muto, J. Chromatogr., 134 (1977) 459–466.
[43] J. Weiss, Ionenchromatographie, VCH Verlagsgesellschaft mbH, Weinheim, 1991, p. 280.
[44] J.R. Larson and C.D. Pfeiffer, Anal. Chem., 55 (1983) 393–396.
[45] V.T. Wee and J.M. Kennedy, Anal. Chem., 54 (1982) 1631–1633.
[46] L. Nitschke, R. Müller, G. Metzner and L. Huber, Fresenius J. Anal. Chem., 342 (1992) 711–713.
[47] C.S. Weiss, J.S. Hazlett, M.H. Datta and M.H. Danzer, J. Chromatogr., 608 (1992) 325–332.
[48] M.T. Calceran, M.C. Carneiro and L. Puignou, Chromatographia, 39 (1994) 581–586.
[49] M. Ahel and W. Giger, Anal. Chem., 57 (1985) 2584–2590.
[50] K. Lemr, M. Zanette and A. Markomini, J. Chromatogr. A, 686 (1994) 219–224.
[51] H. Rothbächer, A. Korn and G. Maier, Tenside Surf. Det., 30 (1993) 165–173.
[52] C. Freeman Allen and L.J. Rice, J. Chromatogr., 110 (1975) 151–155.
[53] I. Zeeman, J. Chromatogr., 363 (1986) 223–230.
[54] P. Jandera, J. Urbánek, B. Prokes and J. Churácek, J. Chromatogr., 504 (1990) 297–318.
[55] Z. Wang and M. Fingas, J. Chromatogr., 637 (1993) 145–156.
[56] E. Forgács and T. Cserháti, J. Chromatogr. A, 661 (1994) 239–243.
[57] P.L. Desbène, B. Desmazieres, J.J. Basselier and L. Minssieux, Chromatographia, 24 (1987) 588–592.
[58] P.L. Desbène and B. Desmazieres, J. Chromatogr. A, 661 (1994) 207–213.
[59] M.C. Allen and D.E. Linder, JAOCS, 58 (1981) 950–957.
[60] G. Martin, Beckman Applications Data, 1990.
[61] Y. Shi and J.S. Fritz, Anal. Chem., 67 (1995) 3023–3027.