Journal of Chromatography, 608 (1992) 375–383
Elsevier Science Publishers B.V., Amsterdam

CHROM. 24 270

Analysis of alkylaromatic sulphonates by high-performance capillary electrophoresis

P. L. Desbène

UA 455, Université de Rouen, LASOC, Institut Universitaire de Technologie, 43 Rue Saint Germain, 27000 Evreux (France)

C. Rony

UA 455, Université P. et M. Curie, Laboratoire de Chimie Organique Structurale, 4 Place Jussieu, 75005 Paris (France)

B. Desmazières and J. C. Jacquier

UA 455, Institut Européen des Peptides, 76000 Rouen (France)

ABSTRACT

The potential of high-performance capillary electrophoresis for the resolution of alkylaromatic sulphonates was investigated. The operating conditions in capillary zone electrophoresis and in micellar electrokinetic chromatography were optimized on a mixture of model molecules synthesized in the laboratory. The two methods appear to be complementary. Capillary zone electrophoresis allows not only an efficient sorting out according to the number of the sulphonic groups, but also allows, using an organic solvent (acetonitrile), a better resolution in unit time of the structural homologues of the alkylbenzene sulphonates than micellar electrokinetic chromatography. On the other hand, the latter method permits the separation of alkylbenzene sulphonate isomers.

INTRODUCTION

In chemical enhanced oil recovery methods such as surfactant flooding and steam foam soaks or drives, surfactants are used to achieve low interfacial tension or to make a viscous foam, respectively. The design of these processes requires a detailed study of the selection and performance of the surfactants. The surfactants usually used for these purposes are sodium alkyl aryl sulphonates made by sulphonation of a refinery stream [1]. These products consist of a mixture of homologuous series, each homologue containing isomers. Moreover, a careful design of the surfactant system is required to tailor is composition to the characteristics of the reservoir in which it is to be applied. Hence a detailed analysis of these complex matrices appears to be essential. Linear alkylbenzene sulphonates (LAS) are anionic surfactants widely used in detergent formulations. Commercial LAS materials are mixtures of various alkyl homologues (which may vary from C_9 to C_{24}) and of phenyl positional isomers [2]. Analytical methods for alkylbenzene sulphonates have therefore received considerable attention. The determination of the alkyl chain distribution of LAS was first carried out by gas chromatography (GC). This method, however, requires the conversion of the LAS into their volatile derivatives before analysis. Desulphonation with acids [3–6], alkali fusion [7], sulphochlorination [8], methylation [9], reduction [10], pyrolysis–GC [11] and acid pyrolysis–GC [12,13] are well known derivati-

Correspondence to: Dr. P. L. Desbène, UA 455, Université de Rouen, LASOC, Institut Universitaire de Technologie, 43 Rue Saint Germain, 27000 Evreux, France.

0021-9673/92/$05.00

zation methods prior to GC. However, high-performance liquid chromatography (HPLC) is currently the most suitable method for the determination of the alkyl chain distribution of LAS, because it does not require the conversion of the LAS into volatile derivatives. LAS have been analysed using reversed-phase chromatography on stationary phases such as C_{18} [14,15], C_8 [15] and C_1 [16], with mobile phases consisting of an aqueous solution of sodium perchlorate, the organic cosolvent being methanol [14], tetrahydrofuran [16] or acetonitrile [14,15]. Mixtures of LAS have also been studied using either ionic suppression [17] [on poly(styrene–divinylbenzene)phases] or ion-pair chromatography (with stationary phases of the C_8 [18] or C_{18} [1,19] type and using the cetrimide or the tetrabutylammonium cation as derivatization reagent).

Some of these techniques, *e.g.* reversed-phase chromatography (with a C_{18} stationary phase and a sodium perchlorate mobile phase) coupled with fluorimetric detection in particular, have allowed in recent years the study of the LAS in aqueous environmental samples [20] and in waste waters [21]. However, the application of these techniques to mixtures of alkylbenzene sulphonates resulting from the sulphonation of petroleum streams, such as WITCO TRS 10–80, appears to be disappointing [19]. Also, ion-exchange chromatography does not allow the resolution of complex industrial mixtures, only into mono-, di- and trisulphonates. No resolution, even partial, is possible with such broad categories of products [22]. In this context, we decided to evaluate the potental of high-performance capillary electrophoresis for the resolution of such mixtures. Taking into account the structures of the products to be analysed, we proceeded with the optimization of the operating conditions on model molecules using either capillary zone electrophoresis (CZE) or micellar electrokinetic chromatography (MEKC).

EXPERIMENTAL

Reagents

Butanol, which was used for the desalting of WITCO TRS 10–80 (WITCO, St. Pierre lès Elbeuf, France), chloroform and methanol, used for its dewaxing, and nitrobenzene and chlorosulphonic acid, used for the sulphonation reaction, were of analytical-reagent grade from Merck (Darmstadt, Germany). *n*-C_2–C_{12}-alkylbenzenes and *n*-, *iso*-, *sec*.- and *tert*.-butylbenzene were of analytical-reagent grade from Aldrich (Strasbourg, France). For analyses by ion-exchange chromatography or high-performance capillary electrophoresis, the methanol and acetonitrile solvents were of RS HPLC grade from Fisons (Rueil-Malmaison, France). The water used for the preparation of the different buffers was systematically purified by reversed osmosis and filtration using a Milli-Ro + Milli-Q system (Millipore, Molsheim, France). The reagents needed for the buffers, *i.e.* sodium tetraborate, boric acid, phosphoric acid and monobasic sodium phosphate were of analytical reagent grade from Prolabo (Paris, France). Sodium dodecyl sulphate (SDS), used in micellar electrokinetic chromatography, was of 99% purity from Sigma (La Verpillière, France).

Apparatus

^1H and ^{13}C NMR spectra were recorded on an AC 200 system (Bruker, Wissembourg, France).

Ion-exchange chromatography was carried out on a PU 4003 chromatograph (Philips, Cambridge, UK) with a 20-μl loop (Rheodyne, Cotati, CA, USA), a PU 4020 detector (Philips) and a Partisil SAX column (Whatman, Clifton, NJ, USA). The signal from the detector was displayed on a Kipp & Zonen (Delft, Netherlands) recorder.

High-performance capillary electrophoresis was performed on a P/ACE 2100 system (Beckman, Fullerton, CA, USA), monitored by a PS/2 computer (IBM, Greenock, UK) using GOLD software (Beckman). Data collection was performed with the same software. The UV detector was set at 214 nm. Injections were performed in the hydrodynamic mode and the injection times were set at 1 or 2 s depending on the sample. The fused-silica capillaries used were of length of 57 cm and I.D. 50 or 75 μm.

The pH values of the buffers were systematically verified before the analyses using a Beckman Model Φ pH meter.

Sulphonation of alkylaromatic compounds

The alkylaromatic compounds were sulphonated using chlorosulphonic acid. The sulphonates were then precipitated as potassium salts following a

protocol adapted from Janczewski and Szczeklik [23] in order to fit the synthesis of small amounts of raw materials and to avoid the problems due to the very variable solubility of the sulphonated compounds depending on the alkyl chain length. In all instances, stoichiometric amounts of chlorosulphonic acid were added. The alkylaromatic compound was dissolved in nitrobenzene (10% solution if the solubility allowed it). The solution was cooled to 5°C and the chlorosulphonic acid was then added dropwise over 30 min, keeping the temperature at 5°C. In cases of small amounts, it was better to dilute the chlorosulphonic acid fivefold with nitrobenzene in order to allow a more regular addition.

The reaction medium was then kept at room temperature for 3 h. With relatively short substituents (chain length $< C_{12}$) a volume of water equal to that of nitrobenzene was added. The solution was then allowed to settle or, if an emulsion was formed, was centrifuged. The organic phase was washed again with the same volume of water. The two aqueous phases were collected, washed with benzene and then neutralized with a 10% potassium carbonate solution. Potassium chloride solution (10%) was then added until the precipitation of the potassium sulphonate was completed. The precipitate was then filtered and dried. The raw product was used without further purification (yield 75–85%).

With long alkyl chain compounds, the sulphonic acid appeared to be insoluble in the water used for its extraction. It was then necessary to neutralize the organic phase directly with 10% potassium carbonate solution with vigorous shaking, adding 10% potassium chloride solution if necessary.

Purification of WITCO TRS 10–80

Mineral salts of the raw sample were precipitated using butanol. The desalted sample was then filtered and the butanol evaporated. At this stage of the purification, it was necessary to remove the non-sulphonated fractions from this complex mixture, almost all of which were alkanes. To do so, we used adsorption liquid chromatography [200 ml of Li-Chrosorb silica (Merck) for 4 g of WITCO TRS 10–80]. The sample was dissolved in *ca.* 10 ml of chloroform. This first fraction was eluted with chloroform and dried, allowing the collection of 0.46 g of waxes. The sulphonated fraction was then eluted from the column with methanol. When the coloured strip corresponding to the polyaromatic compounds had been totally eluted, the methanol solution was vacuum concentrated, allowing the collection of 3.48 g of sulphonated compounds.

RESULTS AND DISCUSSION

As the ion-echange chromatography of the purified WITCO TRS 10–80 indicated that this mixture was constituted almost entirely of monosulphonated compounds (Fig. 1), we then used monosulphonated alkylbenzenes (synthesized in our laboratory) as model compounds. The model compounds were linear alkylbenzene sulphonates with alkyl chain lengths from C_2 to C_{12}, as the ^1H and ^{13}C NMR spectra did not show evidence of very long linear chains, and all the butylbenzene sulphonate isomers, *i.e.*, *n*-, *iso*-, *sec.*- and *tert.*-butylbenzene sulphonates.

Taking into account the structure of the products and the very high performance of capillary electrophoresis, we first undertook the study of the behaviour of these model mixtures using CZE.

Capillary zone electrophoresis of linear alkylbenzene sulphonates

We used a borate–boric acid buffer at a fixed pH of 9 and studied the influence of the variation of the ionic strength on the resolution of such a mixture.

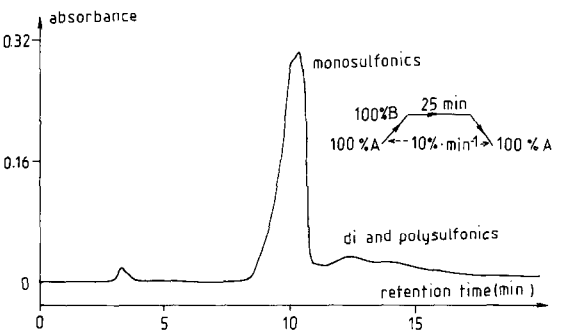

Fig. 1. Analysis of dewaxed WITCO TRS 10–80 by ion-exchange liquid chromatography. Partisil SAX column (25 × 0.46 cm I.D.), d_p = 10 μm; UV detection at 254 nm; flow-rate 0.8 ml/min; injection, 20 μl of a 1% solution of WITCO TRS 10–80 in acetonitrile. Elution gradient: solvent A, water–methanol–acetonitrile (1:1:1); solvent B, aqueous solution of dibasic sodium phosphate–methanol–acetonitrile (1:1:1).

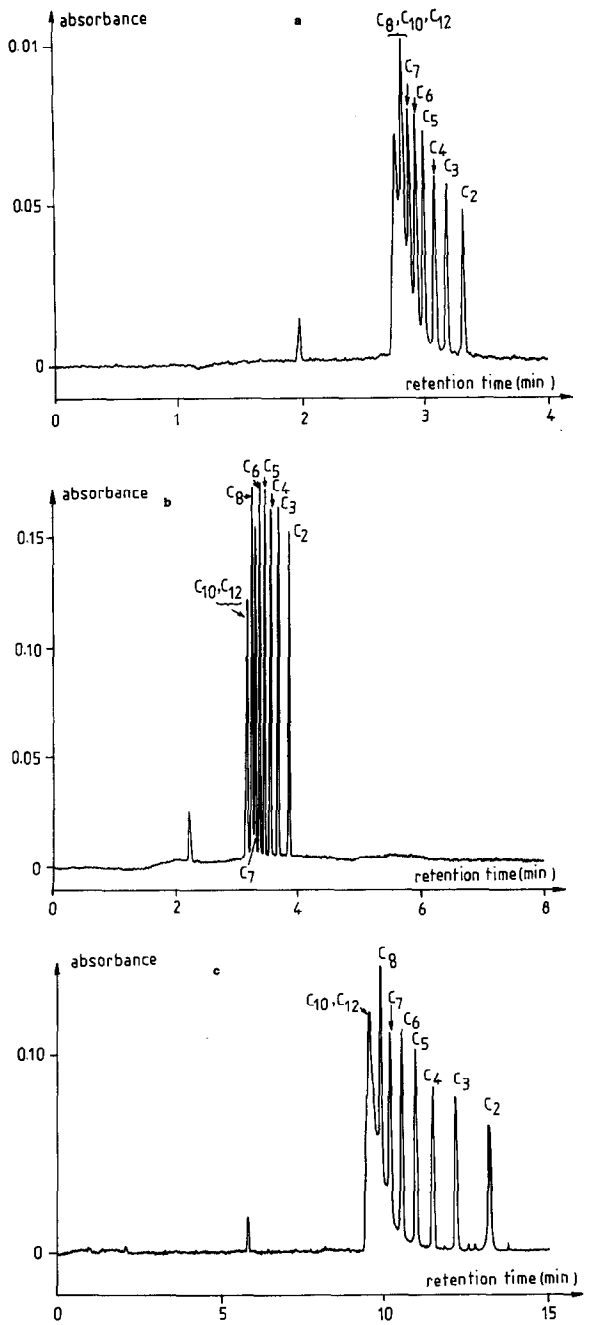

Fig. 2. Electropherograms of LAS mixture obtained by CZE. Fused-silica capillary (57 cm × 75 μm I.D.); temperature, 30°C; hydrodynamic injection, 1 s; detection, 214 nm; borate–boric acid buffer (pH 9). (a) Buffer concentration $6.25 \cdot 10^{-3}$ *M*, applied voltage 30 kV; (b) buffer concentration $12.5 \cdot 10^{-3}$ *M*, applied voltage 30 kV; (c) buffer concentration $25 \cdot 10^{-3}$ *M*, applied voltage 15 kV.

The capillary used was 57 cm × 75 μm I.D., allowing us to work using voltages from 15 to 30 kV, depending on the buffer concentration. Three buffer concentrations were studied, $6.25 \cdot 10^{-3}$, $12.5 \cdot 10^{-3}$ and $25 \cdot 10^{-3}$ *M*. The electropherograms corresponding to the analyses of this mixture of model compounds under each of these operating conditions are shown in Fig. 2.

It appears that the optimum buffer concentration, giving the best resolution in unit time, is $12.5 \cdot 10^{-3}$ *M*. At this concentration, all the alkylbenzene sulphonates are fully separated except for the *n*-decyl- and *n*-dodecylbenzene sulphonate pair. This result is explained by the fact that this concentration still allows us to work with a high applied voltage (30 kV) while the electroosmotic flow is already low compared with that when the buffer concentration is lower ($6.25 \cdot 10^{-3}$ *M*). On the other hand, with a higher buffer concentration ($25 \cdot 10^{-3}$ *M*), even if the electroosmotic flow is then lower, the resolution of the mixture is worse because, taking into account the increased conductivity of the liquid medium, the applied voltage must be lowered from 30 to 15 kV, which means that the elution times will be much longer and the peaks much broader owing the thermal agitation.

In order to resolve completely this mixture of model alkylbenzene sulphonates and so to separate the *n*-decyl- and *n*-dodecylbenzene sulphonates, we studied the influence of the addition of an organic solvent, acetonitrile in particular, on the electrophoretic behaviour of the compounds. Adding an organic solvent makes the liquid medium more hydrophobic, and one can hope to modify the conformations of the compounds and thus to modify their relative electrophoretic mobilities. Acetonitrile was chosen as the organic solvent because of its well adapted characteristics: high dielectric constant, lypophilicity and good transmittance at low wavelengths in the UV region. We therefore added acetonitrile in 5% steps, keeping the buffer pH at 9 and its concentration at $12.5 \cdot 10^{-3}$ *M*, corresponding to the optimum ionic strength.

As the electroosmotic flow is systematically lowered with the addition of acetonitrile, the evolution of the elution times of the different LAS cannot be directly translated into the evolution of their electrophoretic mobility. In order to visualize such an evolution, we calculated the pseudo-capacity fac-

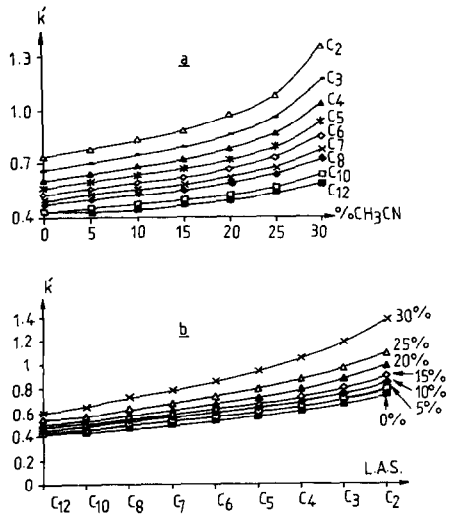

Fig. 3. Influence of acetonitrile content in the liquid medium on the electrophoretic mobility of the LAS constituting the model mixture. Borate–boric acid buffer, $12.5 \cdot 10^{-3}$ *M* (pH 9); fused-silica capillary (57 cm × 50 μm I.D.), voltage, 30 kV; detection, 214 nm; hydrodynamic injection, 2 s. (a) Evolution of the pseudo-capacity factors with the acetonitrile content for the nine studied LAS; (b) evolution of the pseudo-capacity factors with the nature of the considered LAS at different acetonitrile concentrations.

tors of the different compounds analysed. The evolution of the pseudo-capacity factors of the nine LAS studied as a function of the acetonitrile content is shown in Fig. 3a.

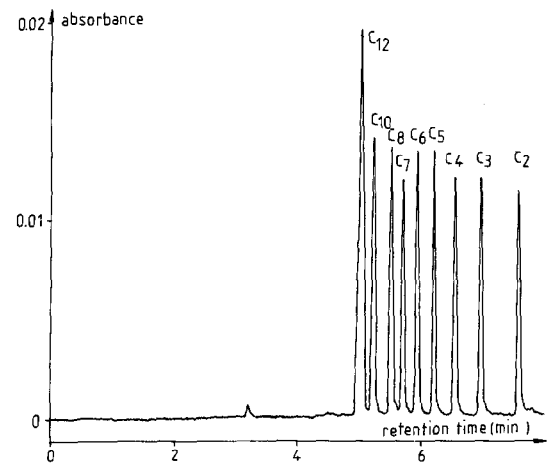

Fig. 4. Electropherogram of the LAS mixture using CZE with an acetonitrile content of 30%. Other conditions as in Fig. 3.

It appears that the electrophoretic mobility of the LAS is lowered on addition of acetonitrile, for each compound. Nevertheless, the extent of this decrease depends on the alkylbenzene sulphonate, as shown in Fig. 3b. Moreover, the selectivity of the electrophoretic system appears to be much more significant when the liquid medium contains 30% of acetonitrile when it contains none.

With the addition of 30% of acetonitrile to the liquid medium, the resolution of the nine alkylbenzene sulphonates is complete as shown on the electropherogram in Fig. 4.

Capillary zone electrophoresis of butylbenzene sulphonate isomers

The industrial mixture WITCO TRS 10–80 should also contain isomers of the linear alkylbenzene sulphonates, and we studied the separation of the four butylbenzene sulphonate isomers as a model.

As with the linear alkylbenzene sulphonates, we first studied the effect of ionic strength on the resolution of this mixture. The concentration used were $6.25 \cdot 10^{-3}$, $12.5 \cdot 10^{-3}$ and $25 \cdot 10^{-3}$ *M*, the pH being kept at 9. As no separation occurs under these conditions, we studied for each buffer concentration the effect of the addition of acetonitrile on the resolution. Again, we obtained very poor results, with only a slight separation with 5% of acetonitrile in a $25 \cdot 10^{-3}$ M buffer.

Hence CZE appears to be useless for the separation of such alkylbenzene sulphonate isomers. As MEKC should be more suitable for the resolution of such a mixture, its use was investigated.

Micellar electrokinetic chromatography of linear alkylbenzene sulphonates

We first studied the influence of the ionic strength, and therefore the influence of the buffer concentration, on the resolution of the model mixture of nine LAS. The SDS concentration was set at $5 \cdot 10^{-2}$ M, the pH of the liquid medium at 9 using borate–boric acid buffer and the applied voltage at 25 kV. Three different buffer concentrations giving three different ionic strengths were tested: $6.25 \cdot 10^{-3}$, $12.5 \cdot 10^{-3}$ and $25 \cdot 10^{-3}$ *M*. The electropherograms obtained are shown in Fig. 5.

The results indicated that the ionic strength corresponding to a buffer concentration of $6.25 \cdot 10^{-3}$

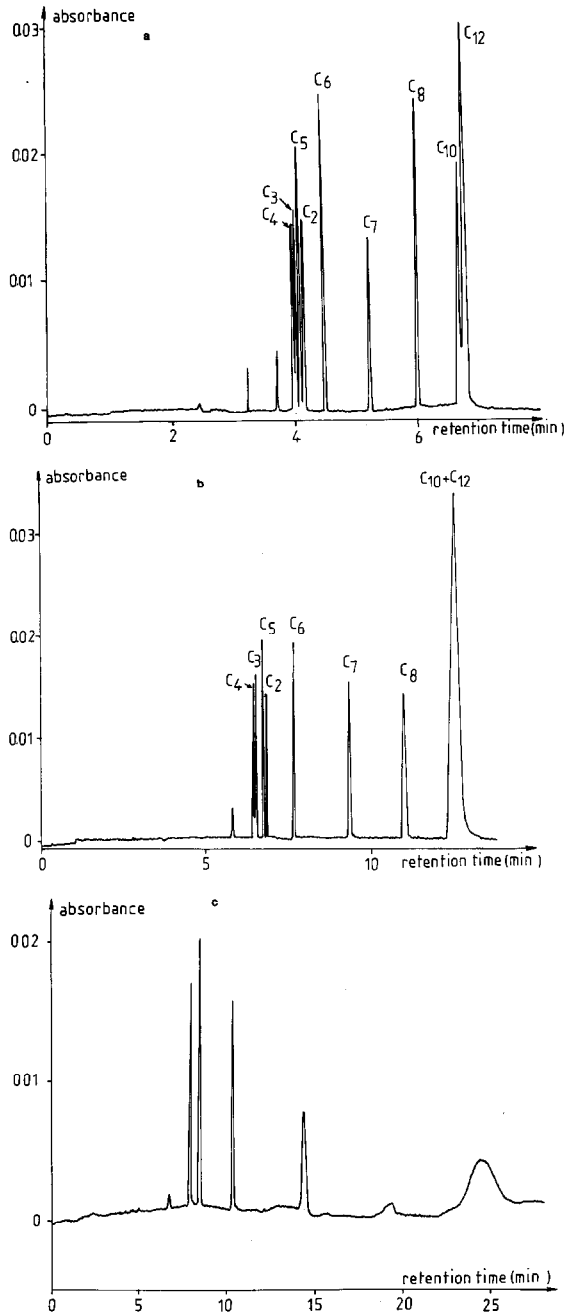

Fig. 5. Study of the influence of ionic strength on the resolution of the LAS mixture using MEKC. Fused-silica capillary (57 cm × 50 μm I.D.); temperature, 30°C; hydrodynamic injection, 2 s; detection, 214 nm; SDS concentration, $5 \cdot 10^{-2}$ *M*; borate–boric acid buffer (pH 9). (a) Borate concentration $6.25 \cdot 10^{-3}$ *M*, applied voltage 25 kV; (b) borate concentration $12.5 \cdot 10^{-3}$ *M*, applied voltage 20 kV; (c) borate concentration $25 \cdot 10^{-3}$ *M*, applied voltage 20 kV.

M is the optimum, allowing virtually a baseline separation for all the compounds except the pairs *n*-butyl- and *n*-propylbenzene sulphonates and *n*-decyl- and *n*-dodecylbenzene sulphonates. We attempted to improve the quality of the separation by studying, at this optimum concentration, the effect of the addition of an organic solvent (acetonitrile) on the resolution.

As shown by the electropherogram in Fig. 6, the addition of acetonitrile improves the resolution of the most hydrophobic LAS. However, this improvement in the resolution of *n*-decyl- and *n*-dodecylbenzene sulphonates is achieved at the expense of a decrease in the quality of separation of the less hydrophobic LAS. In fact, the resolution was poorer than that with no acetonitrile present for both the *n*-butyl and *n*-propylbenzene sulfonates and the *n*-pentyl and *n*-ethylbenzene sulphonates pairs (compare Figs. 5a and 6). Hence MEKC appears to be inferior to CZE for LAS.

Micellar electrokinetic chromatography of butylbenzene sulphonate isomers

We investigated the optimization of the ionic strength in separation of the model mixture of four butylbenzene sulphonates isomers. All the other parameters, *i.e.*, the applied votage, pH and SDS concentration, were identical with those for the optimization of the resolution of the LAS model mixture using MEKC. As shown in Fig. 7a, a slight separation is obtained with buffer concentration of

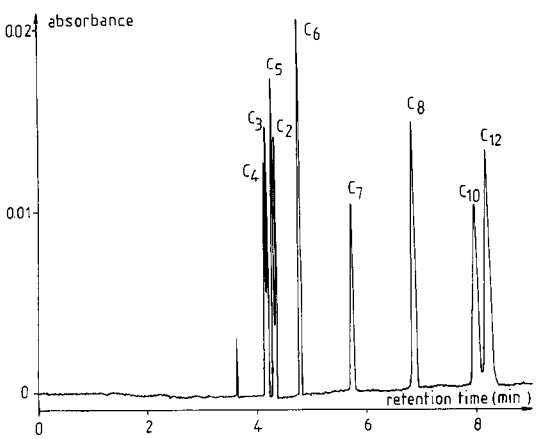

Fig. 6. Influence of acetonitrile content in the liquid medium on the MEKC behaviour of the LAS constituting the model mixture. Acetonitrile content, 5%; other conditions as in Fig. 5a.

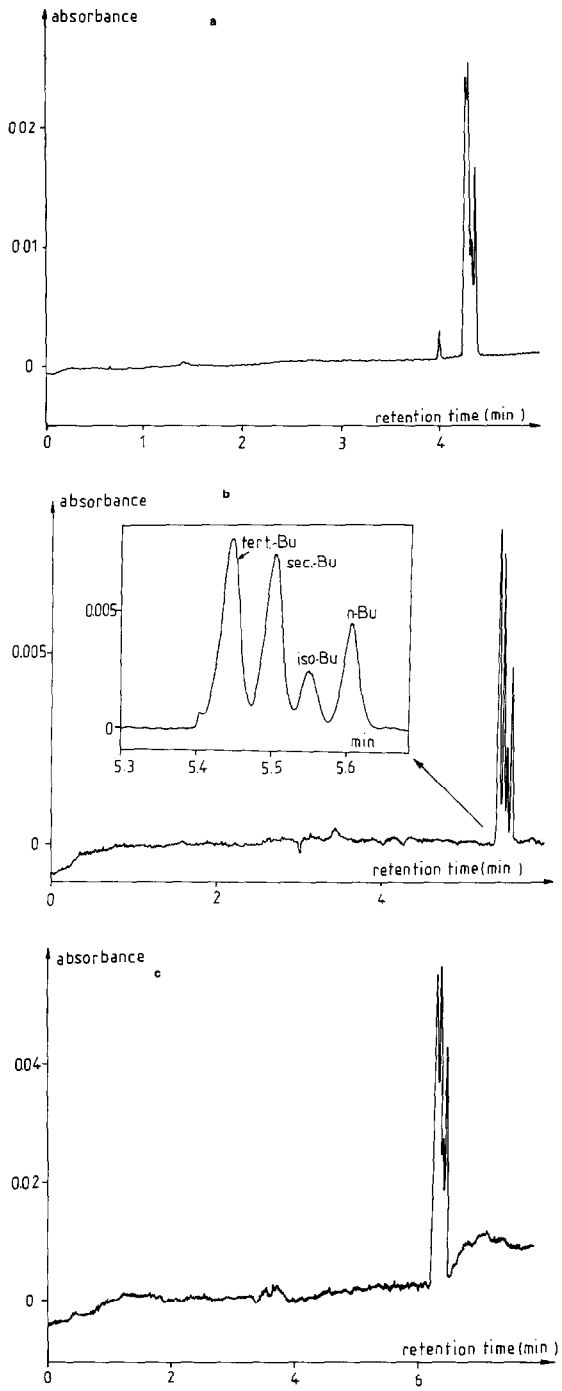

Fig. 7. Separation of the butylbenzene sulphonate isomers using MEKC. Study of the influence of the addition of an organic solvent (acetonitrile) on the separation. Acetonitrile content: (a) 0%, (b) 10% and (c) 10%. Other conditions as in Fig. 5a. Bu = butyl.

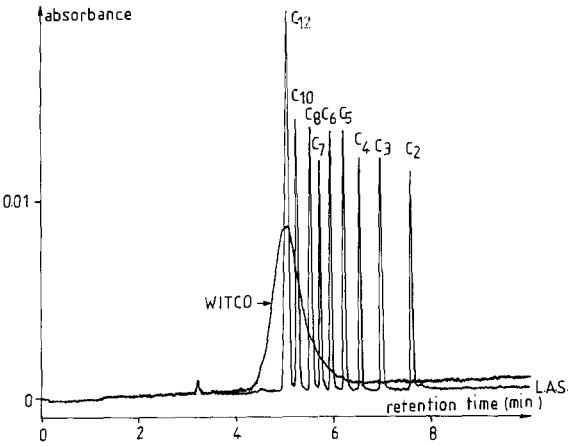

Fig. 8. Comparison of the electrophoretic behaviours of WITCO TRS 10–80 and the model LAS using CZE with the optimized operating conditions for the separation of the LAS mixture (for operating conditions, see Fig. 4).

$6.25 \cdot 10^{-3}$ *M*. For higher buffer concentrations, all the butyl isomers co-eluted.

As we could not achieve a satisfactory separation by varying only the ionic strength of the liquid phase, we studied the influence of the addition of acetonitrile on the resolution. The electropherograms obtained with additions of 10 and 15% of acetonitrile are shown in Fig. 7b and c, respectively. The results showed that the optimum concentration of acetonitrile in the liquid medium is 10%. Fig. 7b shows that the four isomers are almost completely separated. Therefore, MEKC appears to be a much more selective technique than CZE for the separation of alkylbenzene sulphonate isomers.

Electrophoretic behaviour of WITCO TRS 10–80

We first investigated this industrial product, which is a complex mixture of alkylaromatic sulphonates, using CZE with the previously optimized conditions for the analysis of LAS. The electropherogram obtained is shown in Fig. 8.

In order to allow a good comparison, Fig. 8 also shows the analysis of the LAS under the same conditions. It appears that WITCO TRS 10–80 gives a broad peak in the elution zone of alkylbenzene sulphonates with alkyl chain lengths between C_6–C_7 and C_{12}. Unfortunately, no fine resolution is obtained with WITCO TRS 10–80. Such a situation is not really surprising, as our study indicated an inability of CZE to resolve isomeric mixtures. As

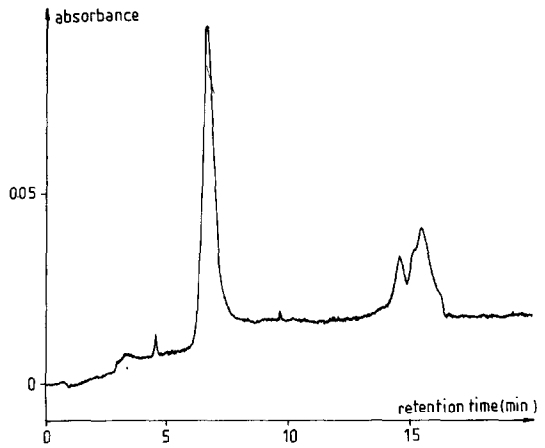

Fig. 9. Electropherogram of WITCO TRS 10–80 using CZE. Fused-silica capillary (57 cm × 50 μm I.D.; temperature, 30°C; hydrodynamic injection, 2 s; borate–boric acid buffer, $25 \cdot 10^{-3}$ *M* (pH 9); acetonitrile content, 10%; detection, 214 nm; voltage, 20 kV.

WITCO TRS 10–80 is obtained by the sulphonation of a petroleum stream, the mixture must contain a large number of isomers for each linear homologue. Despite the high performance of capillary electrophoresis, a satisfactory analysis of this complex mixture was not obtained.

Starting from these operating conditions, we tried to improve the resolution of WITCO TRS 10–80, modifying the ionic strength and therefore the sodium tetraborate concentration and also the acetonitrile content. The electropherogram obtained is shown in Fig. 9.

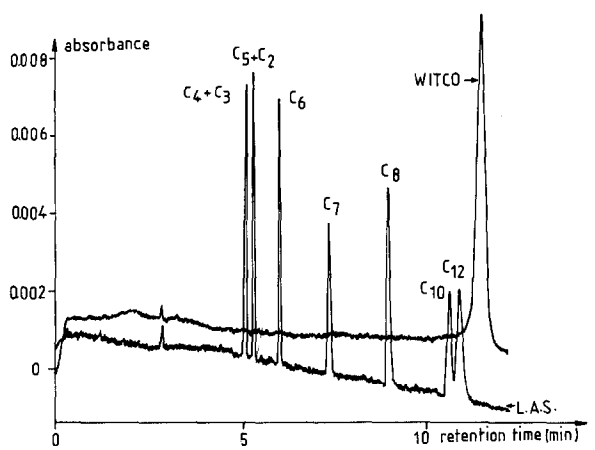

Fig. 10. Comparison of the electrophoretic behaviours of WITCO TRS 10–80 and the model LAS using MEKC. Fused-silica capillary (57 cm × 50 μm I.D.); temperature, 30°C; hydrodynamic injection, 2 s; borate–boric acid buffer, $6.25 \cdot 10^{-3}$ *M* (pH 9); acetonitrile content, 5%; SDS concentration, $5 \cdot 10^{-2}$ *M*; detection 214 nm; voltage, 25 kV.

Compared with the first analysis, WITCO TRS 10–80 now appeared to be a much more complex mixture. In addition to the peak previously found, this electropherogram reveals the presence of four more peaks more or less resolved. Obviously, the products corresponding to these peaks have electrophoretic mobilities clearly higher than those of the alkylbenzene monosulphonates.

Finally, we analysed WITCO TRS 10–80 using MEKC as this technique should allow the resolution not only of the homologous mixture but also of the isomers. The electropherogram for the separation of WITCO TRS 10–80 under the the previously optimized conditions for the separation of the linear alkylbenzene sulphonates is shown in Fig. 10. For comparison, the electropherogram obtained for the separation of the LAS is also shown.

This MEKC analysis confirms the results obtained by CZE, *i.e.* WITCO TRS 10–80 contains alkylaromatic sulphonates with relatively long chains. Nevertheless, because of the presence of numerous isomers, a fine resolution cannot be obtained, as the compounds constituting WITCO TRS 10–80 have elution times close to the micelle one. Effectively, the elution time of the micelle under these operating conditions was measured using Sudan III as 13 min. Under such conditions, the interactions of the analysed products with the hydrophobic micellar core are too strong and do not allow a satisfactory selectivity to reveal more or less individually the constituents.

CONCLUSION

It appears that CZE is more selective than MEKC for the separation of linear alkylbenzene sulphonates. On adding an organic solvent (acetonitrile) to the liquid medium, a baseline separation is obtained in less than 4 min for all the studied LAS (alkyl chain lengths between C_2 and C_{12}). Therefore, the analysis time is at least three times shorter compared with HPLC.

Even if MEKC appears to be less efficient than CZE for the separation of the homologous LAS mixture, it has an advantage over the latter as it

allows the resolution of alkylbenzene sulphonates isomers.

CZE and MEKC appear to be complementary techniques in the present context. Their application to the resolution of an industrial formulation (WITCO TRS 10–80) allowed us to confirm several characteristics of this complex matrix (sulphonated petroleum cut). The studies performed using either technique demonstrated that this mixture is essentially constituted of monosulphonated alkylbenzenes with relatively long alkyl chains and with a narrow distribution. Nevertheless, the presence in this mixture of numerous isomers did not allow us to obtain a good resolution and identification. The coupling of capillary electrophoresis with mass spectrometry should allow us to improve the characterization and the identification of this complex surfactant mixture.

REFERENCES

1 P. D. Pols and W. G. M. Afterof, in, *Proceedings of the 1985 SPE International Symposium on Oilfield and Geothermal Chemistry*, Society of Petroleum Engineers of AIME, Richardson, TX, 1985, Paper SPE 13571, p. 231.
2 A. Marcomini and W. Giger, *Anal. Chem.*, 59 (1987) 1709.
3 J. D. Knight and R. House, *J. Am. Oil Chem. Soc.*, 36 (1959) 195.
4 E. A. Sitzkorn and A. B. Carel, *J. Am. Oil Chem. Soc.*, 40 (1963) 57.
5 S. Lee and N. A. Puttman, *J. Am. Oil Chem. Soc.*, 44 (1967) 158.
6 H. Y. Lew, *J. Am. Oil Chem. Soc.*, 14 (1972) 665.
7 S. Nishi, *Bunseki Kagaku*, 14 (1965) 917.
8 S. Watanabe, M. Nukiyama, F. Takagi, K. Iida, T. Kaise and Y. Wada, *Shokuhin Eiseigaku Zasshi*, 16 (1975) 212.
9 M. Imaida, T. Suminoto, M. Yada, M. Yoshida, K. Koyama and N. Kunita, *Shokuhin Eiseigaku Zasshi*, 16 (1975) 218.
10 S. Matsutani, T. Shige and T. Nayai, *Yukagaku*, 28 (1979) 847.
11 T. H. Lidicoet and L. H. Smithson, *J. Am. Oil. Chem. Soc.*, 42 (1965) 1097.
12 H. Y. Lew, *J. Am. Oil Chem. Soc.*, 44 (1967) 359.
13 R. Denig, *Tenside Deterg.*, 10 (1973) 59.
14 A. Nakae, K. Tsuji and M. Yamanaka, *Anal. Chem.*, 52 (1980) 2275.
15 A. Marcomini and W. Giger, *Anal. Chem.*, 59 (1987) 1709.
16 M. A. Castles, B. L. Moore and S. R. Ward, *Anal. Chem.*, 61 (1989) 2534.
17 A. Nakae and K. Kunihiro, *J. Chromatogr.*, 152 (1978) 137.
18 D. Thomas and J. L. Rocca, *Analusis*, 7 (1979) 386.
19 L. A. Verkruyse, R. V. Lewis, K. O. Meyers and S. J. Salter, in, *Proceedings of the 1983 SPE International Symposium on Oilfield and Geothermal Chemistry*, Society of Petroleum Engineers of AIME, Richardson, TX, 1983, Paper SPE 11781, p. 105.
20 A. Di Corcia, M. Marchetti, R. Samperi and A. Marcomini, *Anal. Chem.*, 63 (1991) 1179.
21 A. Marcomini, S. Capri and W. Giger, *J. Chromatogr.*, 403 (1987) 243.
22 F. E. Suffridge and D. L. Taggart, in, *Proceedings of the 1977 SPE International Symposium on Oilfield and Geothermal Chemistry*, Society of Petroleum Engineers of AIME, Richardson, TX, 1977, Paper SPE 6596, p. 75.
23 M. Janczewski and H. Szczeklik, *Rocz. Chem.*, 35 (1961) 369.