ELSEVIER

Journal of Chromatography A, 689 (1995) 107–121

JOURNAL OF CHROMATOGRAPHY A

# Determination by high-performance capillary electrophoresis of alkylaromatics used as bases of sulfonation in the preparation of industrial surfactants☆

P.L. Desbène[a,b,*], C.M. Rony[a,b]

[a]*Laboratoire d'Analyse des Systèmes Organiques Complexes, Université de Rouen, IUT, 43 Rue Saint Germain, 27000 Evreux, France*

[b]*IRFMP, Université de Rouen, 76134 Mont Saint Aignan Cédex, France*

First received 30 January 1994; revised manuscript received 1 August 1994

**Abstract**

Having previously attempted to determine by high-performance capillary electrophoresis (HPCE) industrial surfactants resulting from the sulfonation of oil fractions (WITCO TRS 10-80), it was decided, because of the complexity of these fractions and of the low resolution obtained, to undertake the analysis by HPCE of mixtures of alkylaromatics used as bases to prepare these compounds. Using a model mixture of alkylbenzenes, including benzene and a series of homologous compounds with alkyl chain lengths of $C_1$–$C_{16}$, the conditions of the separation were optimized. It was shown that it is possible to analyse this mixture, with total baseline resolution, in 35 min using simultaneously sodium dodecyl sulfate and an organic co-solvent at high concentrations. These conditions also allow the resolution not only of the alkylated compounds used as the bases for the preparation of industrial alkylbenzenesulfonates (Sulframine ACB and Sulfo TPB) but also the surfactants themselves. It must also be noted that these conditions, transposed to WITCO TRS 10-80, allow for the first time the resolution of this complex mixture.

## 1. Introduction

Surfactants are amphiphilic compounds, which results in the peculiar properties of these molecules, such as adsorption at interfaces, formation of micelles in solution and the decrease in surface tension. Consequently, these chemicals are often used as wetting or foaming agents, emulsifiers or detergents.

Linear alkylbenzenesulfonates (LAS), which are the main bases of surfactants for domestic use (with a 1.2 million tons a year production, i.e. 24% of the world production of surfactants), have frequently retained the attention of analysts. At first, the distribution of their alkyl chains was determined using gas chromatography. However, this technique requires preliminary conversion of LAS into volatile compounds. This derivatization can be performed via various reactions: desulfonation using acids [1–4], alkaline fusion [5], sulfochlorination [6],

* Corresponding author. Address for correspondence: Laboratoire d'Analyse des Systèmes Organiques Complexes, Université de Rouen, IUT, 43 Rue Saint Germain, 27000 Evreux, France.

☆ Presented at the *6th International Symposium on High Performance Capillary Electrophoresis, San Diego, CA, 31 January–3 February 1994.*

0021-9673/95/$09.50 
*SSDI* 0021-9673(94)00739-X

methylation [7], reduction to alkylthiophenols [8], pyrolysis [9] or acidic pyrolysis [10,11].

In order to avoid the systematic conversion of LAS into volatile compounds, these complex mixtures are now generally determined by a high-performance liquid chromatography, and different chromatographic systems have been proposed. LAS have been determined by reversed-phase partition liquid chromatgraphy, using various stationary phases such as $C_{18}$ [12,13], $C_8$[13] or $C_1$ [14] bonded silicas, the mobile phase being in most instances an aqueous solution of sodium perchlorate with methanol [12], acetonitrile [12,13] or tetrahydrofuran [14] as co-solvent. Using such a chromatographic system, with fluorimetric detection, Marcomini and co-workers [15,16] determined LAS at very low concentrations in fluvial waters. On the other hand, the determination of alkylbenzenesulfonates has been also studied either by ion suppression using polymeric stationary phases [17], or by ion-pair chromatography with $C_8$ [18] or $C_{18}$ [19] bonded silica stationary phases, using tetrabutylammonium or cetrimide as counter ion. Recently, Chen and Pietrzyk [20] separated industrial LAS not only as a function of homologous series, but also as a function of positional isomerism by reversed-phase partition chromatography, using $C_{18}$ bonded silica stationary phase. To achieve this separation, after studying different alkali and alkaline earth metal cations, they used high concentrations of sodium chloride and proceeded to a double elution gradient, increasing the acetonitrile content and decreasing the ionic strength. Unfortunately, these chromatographic techniques, and also ion-exchange chromatography, give disappointing results in the determination of industrial anionic surfactants resulting from the sulfonation of oil fractions [19,21].

Consequently, we considered some years ago studying the determination of alkylbenzenesulfonates by high-performance capillary electrophoresis [22], and also capillary zone electrophoresis (CZE) and micellar electrokinetic chromatography (MEKC). Other workers [23] have studied the separation of sulfate and sulfonate surfactants by isotachtophoresis. Romano et al. [24] analysed an alkylsulfonates mixture by CZE using indirect UV detection.

Although MEKC, in contrast to CZE, allows the resolution of homologous alkylbenzenesulfonates and also of positional isomers [22], the application of this technique to the determination of anionic surfactants resulting from the sulfonation of oil fractions, such WITCO TRS 10-80, is disappointing because of the extreme complexity of these mixtures [22]. As the difficulty is due, at least partially, from the great complexity of the hydrophobic part of the surfactant amphiphilic components, an answer should be sought from the study of the alkylates used as bases for the sulfonation. Consequently, we decided to study the analysis of these raw materials by capillary electrophoresis and more precisely, because of the chemical characteristics of these complex mixtures, by MEKC and, as second step, to apply the operating conditions found to the determination of industrial anionic surfactants.

## 2. Experimental

### 2.1. Reagents

The water required for the preparation of buffers was systematically purified by reversed osmosis and filtration using a Milli-RO + Milli-Q system (Millipore, Molsheim, France). The buffer reagents, sodium tetraborate (decahydrate), boric acid and sodium monobasic phosphate, were of analytical-reagent grade from Aldrich, France (La Verpillère, France).Buffers were obtained from concentrated solutions prepared daily, and the pH was controlled systematically before use. Sodium dodecyl sulfate (SDS) was of 99%$^+$ grade from Sigma France (St. Quentin de Fallavier, France). The different organic solvents used, both for the high-performance capillary electrophoresis (HPCE) analyses (i.e., acetonitrile, acetone, methanol and 2-propanol) and for the purification of some samples such as WITCO TRS 10-80 (i.e., chloroform and butanol) were

of RS HPLC grade (Carlo Erba, Rueil Malmaison, France) and were used as received.

### 2.2. Apparatus

All experiments were carried out on a P/ACE 2100 system (Beckman, Fullerton, CA, USA) monitored by a PS/2 computer (IBM, Greenock, UK) using P/ACE software (Beckman). Data collection was performed with the same software. Samples were loaded by pressure injection (injection time 1 or 2 s) into a fused-silica capillary (57 cm × 50 μm I.D.). UV detection was performed at 214 nm, through the capillary at 50 cm from the inlet. The pH values were measured using a Beckman Model Φ pH meter at the analysis temperature. The electroosmotic flow was systematically determined by injection of methanol or acetone, the migration time of micelle being estimated to 4.5 times the migration time of the electroosmotic flow [25]. Effectively, because of the elution of the most lipophilic alkylbenzenes with the micelle, the direct determination of the micelle migration time was often impossible.

### 2.3. Samples

The alkylbenzenes used as model molecules were of 99% grade, from Aldrich, and were injected without further purification.

The industrial anionic surfactants studied, i.e., WITCO TRS 10-80, WITCO Sulframine AcB and WITCO Sulfo TPB, and also their bases of sulfonation, linear dodecylbenzene and the tetrapropylbenzene, were kindly furnished by WITCO France (St. Pierre les Elbeuf, France). These industrial compounds were subjected to analysis without further purification, with the exception of WITCO TRS 10-80, which was desalted and dewaxed according to the procedure reported below.

As the raw sample contained some mineral salts, the latter were precipitated by addition of butanol. The desalted product was obtained after filtration and evaporation of the butanol. As this product contains non-sulfonated fractions, it was necessary to eliminate them in order to complete the purification. This was performed using adsorption liquid chromatography on silica. A 2.5 cm I.D. column containing 200 ml of LiChrosorb silica, $d_p$ = 20–50 μm (Merck, Darmstadt, Germany), was used to dewax a 4-g sample of WITCO TRS 10-80. The desalted sample was dissolved in 10 ml of chloroform and was deposited at the column inlet. Waxes were eluted with 300 ml of chloroform. After evaporation of the chloroform, there remained 0.46 g of waxes. The sulfonated fraction was then eluted with methanol. Elution was performed until the total migration of a coloured band corresponding to the polyaromatic fraction. After concentration, 3.48 g of sulfonated compounds remained.

## 3. Results and discussion

As the alkylaromatic organic matrices used as raw materials for the preparation of industrial anionic surfactants are very complex mixtures of hydrophobic compounds, we first examined the optimization of their analysis by MEKC by studying the electrophoretic behaviour of model molecules.

### 3.1. Study of the electrophoretic behaviour of model alkylbenzenes in micellar electrokinetic chromatography

The model mixture was composed of alkylbenzenes, including benzene and $C_1$–$C_{16}$ homologous compounds. We used $Na_2B_4O_7$–$NaH_2PO_4$ buffer adjusted at pH 9 in order to operate in the presence of an important electroosmotic flow and to obtain fast separations with maximum efficiency.

According to Terabe [25] and Vindevogel and Sandra [26], we examined successively the influence on the resolution of the concentration of SDS, the ratio of organic co-solvents, the ionic strength in the mobile phase and the nature of the organic co-solvent.

*Influence of sodium dodecyl sulfate concentration on the resolution of a model mixture of alkylbenzenes*

With electrolyte ionic strength kept constant (25 m*M* $Na_2B_4O_7$–50 m*M* $NaH_2PO_4$ buffer, pH 9) we first studied the influence of the SDS concentration in order to optimize the capacity factors. Effectively, according to Terabe [25] and Vindevogel and Sandra [26], the resolution by time unit is maximum when the capacity factors of the analytes are in the range 0.5–10. As the critical micellar concentration of SDS is 8 m*M* in water at 25°C, we studied an SDS concentration range of 12.5–50 m*M*.

From this series of experiments, it appears that the optimum SDS concentration is 25 m*M*. Effectively, at a higher SDS concentration (50 m*M*), only alkylbenzenes with a chain shorter than three carbons are resolved, the more hydrophobic alkylbenzenes eluting as a poorly resolved signal with too high capacity factors ($k' > 10$). In contrast, with a 25 m*M* concentration of SDS, as reported in Fig. 1, a good resolution in time units is obtained for alkylbenzenes with side-chains of short and medium lengths, with capacity factors of 1.7–4. However, as a result of the relatively narrow separation range, alkylbenzenes with chain lengths longer than $C_7$ are not resolved. These compounds, which have a great affinity for micelles, elute as a single, broad peak.

However, a lower SDS concentration (12.5 m*M*) does not allow the resolution of alkybenzenes with alkyl chains longer than $C_7$ to be

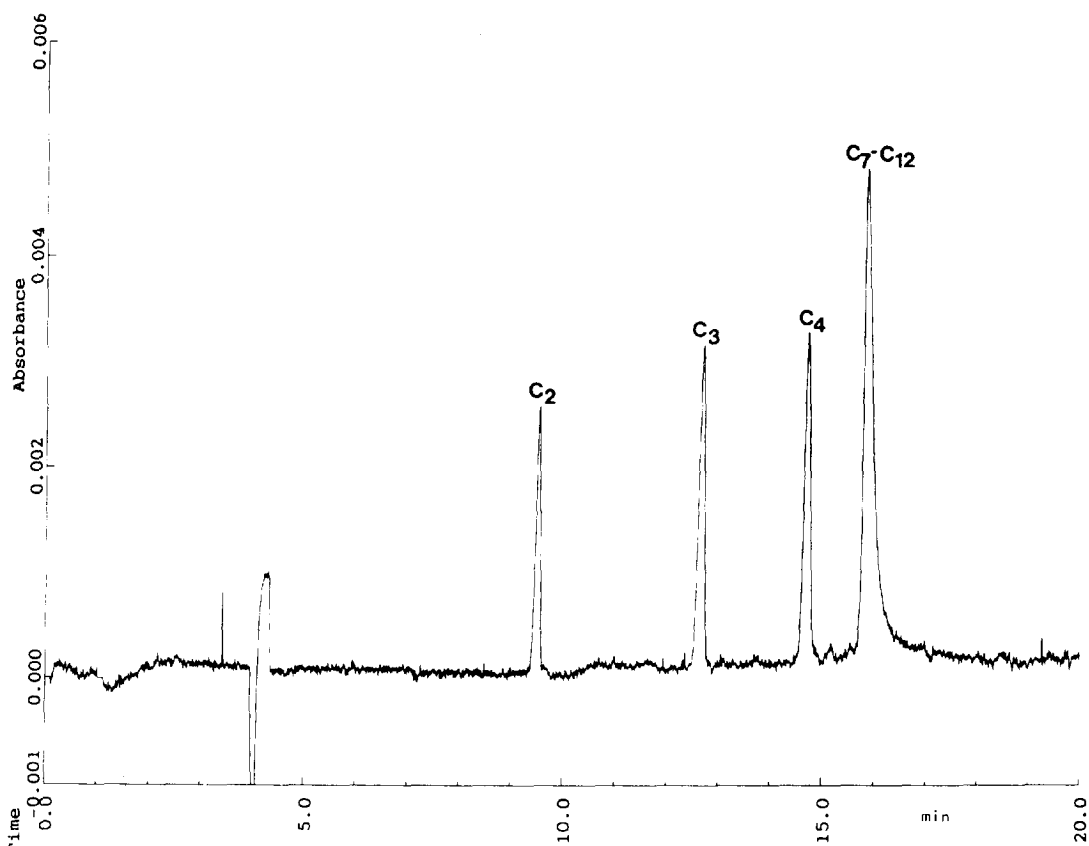


Fig. 1. Influence of SDS concentration on the resolution of a mixture of model alkylbenzenes. Operating conditions: electrolyte, 50 m*M* $NaH_2PO_4$–25 m*M* $Na_2B_4O_7 \cdot 10H_2O$ buffer (pH 9); [SDS], 25 m*M*; temperature, 30°C; applied voltage, 20 kV; hydrodynamic injection, 1 s; detection at 214 nm.

improved but an important loss of resolution in time units is observed for alkylbenzenes with short chains ($C_1$, $C_2$) as their capacity factors become too small.

Consequently, it seems impossible to achieve a satisfactory resolution of alkylbenzenes with alkyl chains lengths greater than $C_7$ by optimizing only the SDS concentration. As an improvement of the separation can result only from a decrease in the strong interactions between the most hydrophobic compounds and the core of the micelles, we studied in a second step the influence of the addition of a co-solvent on the resolution of our model mixture of alkylbenzenes. Such a strategy was likely to modify the partition coefficients of the solute molecules between the mobile phase and the pseudo-stationary phase, thus allowing the capacity factors to be modified and also the electroosmotic flow velocity and therefore the migration-time window to be changed.

*Influence of mobile phase polarity on the resolution of a model mixture of alkylbenzenes*

With the SDS concentration kept at the optimum value of 25 m*M*, we studied the influence of increasing the co-solvent concentration on the quality of separation of the model alkylbenzene mixture. We chose acetonitrile as organic co-solvent because of its low viscosity and its relatively high dielectric constant. According to Schwer and Kenndler [27], the electroosmotic flow velocity decreases and the analysis times increase if the viscosity of the electrophoretic medium increases and/or if the dielectric constant of the mobile phase decreases. Consequently, the electroosmotic flow and the electrophoretic system performances will be less perturbed by acetonitrile than by other organic solvents.

A range of acetonitrile concentration of 5–60% was studied in 5% increments. It was found that the addition of small amounts of acetonitrile does not improve the separation of the most hydrophobic compounds (alkylbenzenes with chain lengths between $C_7$ and $C_{12}$). A rough separation begins for a concentration of 30% of acetonitrile and an acceptable resolution of the whole alkylbenzene model mixture is obtained with about 45% of acetonitrile (Fig. 2a).

Obviously, for such concentrations of acetonitrile, and in agreement with Bullock [28], there are no more micelles in the electrophoretic medium [29] and under such conditions the different electrophoretic mobilities allowing the separation of alkylbenzenes can result only from hydrophobic interactions between the alkylbenzene molecules and the SDS, i.e., by solvatophoby according to the principle developed by Walbroehl and Jorgenson [30].

However, it must be noted that for such a concentration of acetonitrile in the mobile phase (Fig. 2a), the peak corresponding to phenyldodecane, i.e., the most hydrophobic component of the mixture, appears relatively broad. As this decrease in the efficiency of the system, in the case of the most hydrophobic compounds, could result from the only partial solubility of these compounds in the mobile phase we performed the analysis with a mobile phase containing 50% of acetonitrile. As indicated by Fig. 2b, this mobile phase allows the efficiency of the electrophoretic system to be increased, as the peaks of the most hydrophobic components are clearly narrower in spite of an increase of the analysis time, which results from a noticeable increase in the electroosmotic flow time ($t_{eo}$), $t_{eo}$ now being 7 min instead of about 6 min previously (Fig. 2a). It is worth noting that under these new operating conditions, baseline resolution is not achieved for all the components of the mixture analysed.

As the resolution seems to increase systematically when the amount of acetonitrile increases, we analysed the model mixture in the presence of a mobile phase containing 60% of acetonitrile. As evidenced by Fig. 2c, two main features appear under these new operating conditions: (i) a new increase in analysis times, resulting from a further decrease in the electroosmotic flow, $t_{eo}$ now being 10 min; and (ii) a general loss of resolution, resulting from insufficient interactions between the analytes and the SDS, as the mobile phase becomes too lipophilic because of the addition of an important amount

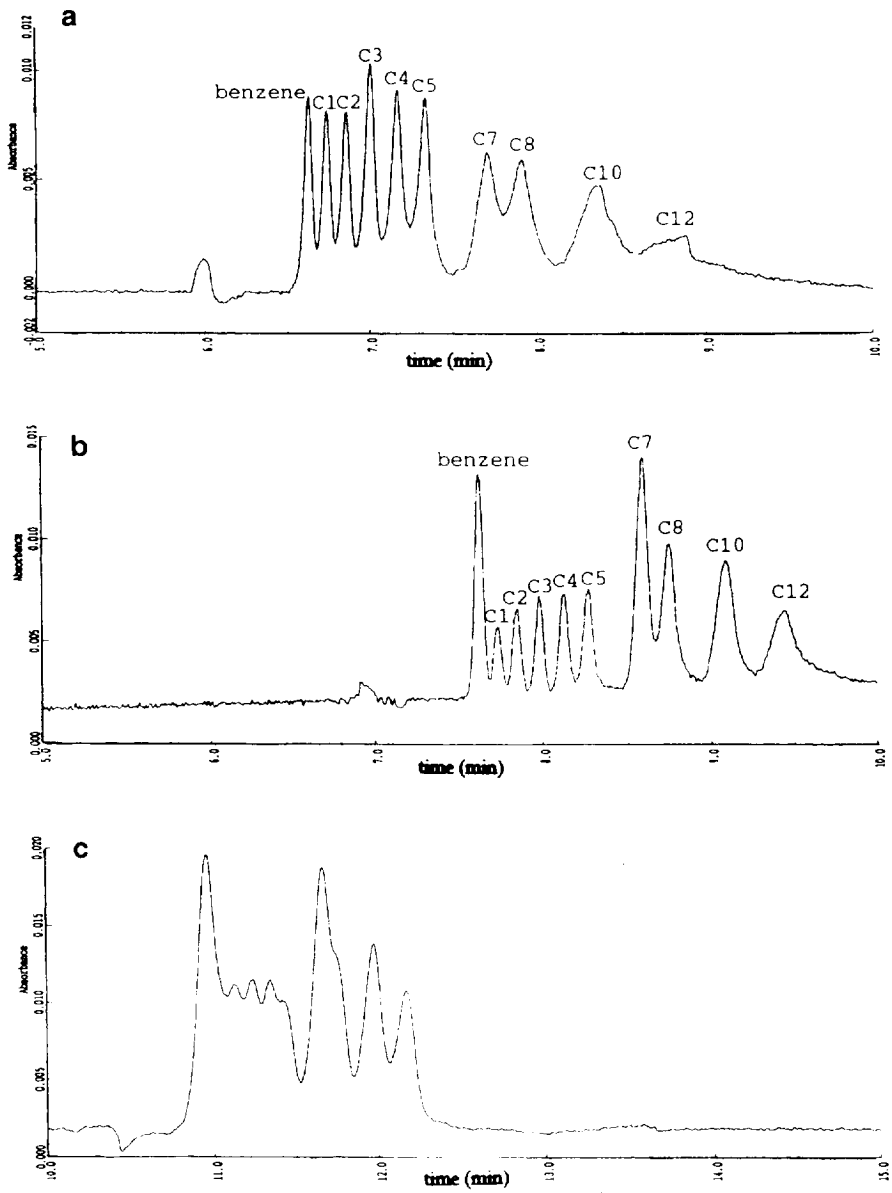


Fig. 2. Influence of the mobile phase polarity on the electrophoretic behaviour of model alkylbenzenes. Operating conditions: electrolyte, 50 m*M* $NaH_2PO_4$–25 m*M* $Na_2B_4O_7 \cdot 10H_2O$ buffer (pH 9); [SDS], 25 m*M*; temperature, 30°C; applied voltage, 30 kV; hydrodynamic injection, 1 s; detection at 214 nm. Acetonitrile concentration: (a) 45; (b) 50; (c) 60% (v/v).

of acetonitrile. Therefore, the optimum amount of acetonitrile in the mobile phase seems to be around 50%.

After optimizing this parameter, and with the resolution appearing to be almost satisfactory for all the components of the model mixture, we attempted to improve the analysis by increasing the volume of the pseudo-stationary phase.

*Influence of the volume of the pseudo-stationary phase on the resolution of a model mixture of alkylbenzenes*

Fig. 3 shows the analysis of the model mixture of alkylbenzenes using an electrophoretic system constituted by 50 m*M* $NaH_2PO_4$–25 m*M* $Na_2B_4O_7$ buffer (pH 9), with 50% of acetonitrile and a 50 m*M* concentration of SDS, i.e., twice the volume of the pseudo-stationary phase used previously. It can be seen that a satisfactory resolution of all the components was obtained for the first time.

In order to improve the resolution in time units, we then studied the influence of the ionic strength of the mobile phase on the electrophoretic behaviour of the model alkylbenzenes.

*Influence of ionic strength on the electrophoretic behaviour of the model alkylbenzenes*

When the ionic strength of the electrolyte in the mobile phase decreases, the electroosmotic flow velocity increases, resulting in a noticeable decrease in the analysis time [31]. Therefore, we attempted to determine the optimum ionic strength, i.e., that leading to the best compromise between analysis time and resolution.

As evidenced by comparison of Figs. 3 and 4a, a noticeable decrease in the analysis time can be obtained without a loss of resolution if the ionic strength of the mobile phase is ten times smaller. However, the electropherogram obtained under these conditions is characterized by serious noise, in spite of thorough degassing of the electrolyte before analysis. Such a phenomenon was observed previously by Vindevogel and Sandra [32] in studies performed with electrophoretic media containing a high percentage of organic solvent. With the exception of the noise problem, the separation obtained under these ionic strength conditions was satisfactory and 5 m*M* $NaH_2PO_4$–2.5 m*M* $Na_2B_4O_7$ (pH 9) buffer with an SDS concentration of 50 m*M* appears to be a near-optimum electrolyte.

As a decrease in the noise could only result from a decrease in the acetonitrile concentration in the mobile phase, we decreased the acetoni-

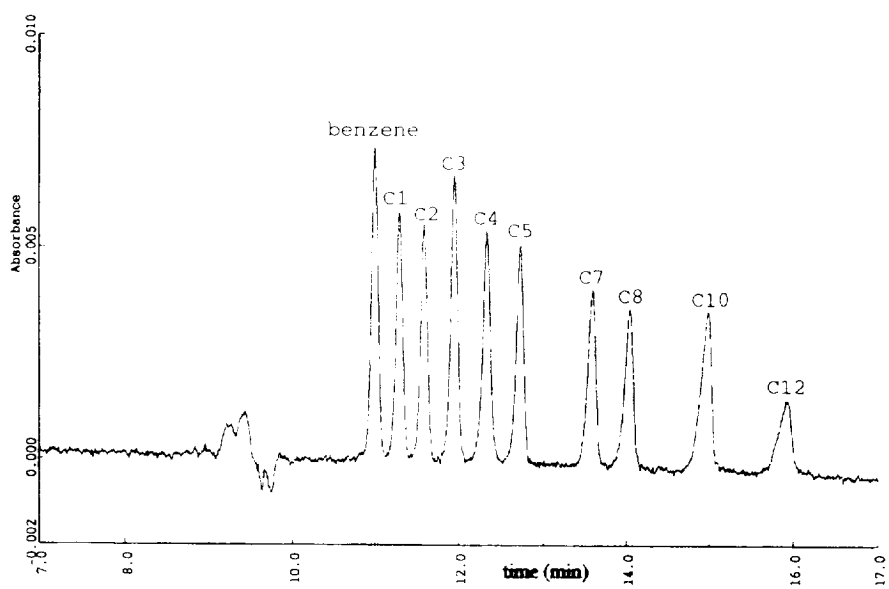


Fig. 3. Influence of an increase in the pseudo-stationary phase volume on the electrophoretic behaviour of model alkylbenzenes. Operating conditions: electrolyte, 50 m*M* $NaH_2PO_4$–25 m*M* $Na_2B_4O_7 \cdot 10H_2O$ buffer (pH 9); [SDS], 50 m*M*; [$CH_3CN$], 50% (v/v); temperature, 30°C; applied voltage, 30 kV; hydrodynamic injection, 1 s; detection at 214 nm.

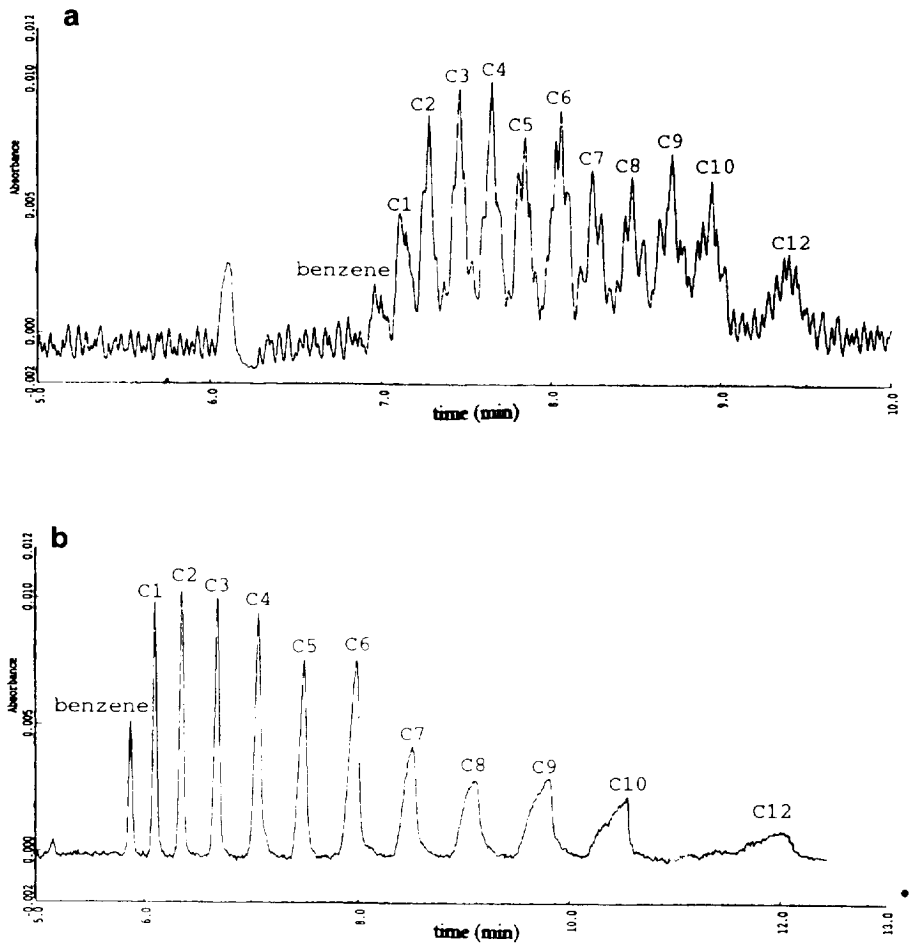


Fig. 4. Influence of the ionic strength of the mobile phase on the electrophoretic behaviour of model alkylbenzenes. Operating conditions: electrolyte, 5 m*M* $NaH_2PO_4$–2.5 m*M* $Na_2B_4O_7 \cdot 10H_2O$ buffer (pH 9); [SDS], 50 m*M*; temperature, 30°C; applied voltage, 30 kV; hydrodynamic injection, 1 s; detection at 214 nm. Acetonitrile concentration: (a) 50; (b) 40% (v/v).

trile content to 40%. As shown by the Fig. 4b, a satisfactory analysis is then obtained: (i) baseline resolution is obtained for the whole series of homologous alkylbenzenes, from benzene to dodecylbenzene; (ii) the analysis time does not exceed 13 min; and (iii) the signal-to-noise ratio is acceptable under these new conditions and a satisfactory sensitivity is obtained.

The only remaining problem is the unsatisfactory resolution of compounds more hydrophobic than dodecylbenzene. Therefore, with a view to improving the resolution of very hydrophobic compounds, we studied the influence of the nature of the mobile phase organic co-solvent on their electrophoretic behaviour.

*Influence of the nature of the organic co-solvent on the resolution of a model mixture of alkylbenzenes*

Modification of the chemical structure of the organic co-solvent should result not only in a change in the electroosmotic flow velocity, but also in a change in the electrophoretic system selectivity [25,26]. Therefore, different co-solvents (acetone, tetrahydrofuran, methanol and 2-propanol) were tested.

This comparative study showed that 2-propanol gives a good thermodynamic selectivity, comparable to that obtained with acetonitrile. Moreover, it presents the advantage of being less polar than the latter. Consequently, it allows one to obtain a suitable hydrophobicity of the electrophoretic medium at lower contents than those previously used with acetonitrile, improving considerably the bad detection previously observed with high concentrations of acetonitrile. In contrast, as 2-propanol has a dielectric constant/viscosity ratio lower than that of acetonitrile, its use as a co-solvent results in a decrease in the electroosmotic flow [27] and an increase in the analysis time. It must be noted that this considerable increase in analysis times, more than 30 min in the case of 2-propanol versus 13 min with acetonitrile, is not a real drawback in the present case, as the quality of analysis is considerably improved when 2-propanol is used. Effectively, as shown in Fig. 5, the use of 2-propanol allows for the first time the complete resolution of all the homologous alkylbenzenes with chain lengths of $C_1$–$C_{16}$ and it is perfectly adapted to the determination of very hydrophobic compounds.

Therefore, we selected 2-propanol as the co-solvent to complete the study, with the following optimum conditions: applied voltage, 30 kV; fused-silica capillary, total length of 57 cm × 50 μm I.D.; mobile phase, 5 m*M* phosphate–2.5 m*M* borax buffer (pH 9) containing 40% of 2-propanol and 50 m*M* SDS; and temperature 30°C. Using these conditions, we analysed industrial mixtures of alkylbenzenes used as bases of sulfonation in the preparation of commercial anionic surfactants and resulting on one hand from the condensation of $C_{12}$-centred α-olefins on benzene, resulting in a mixture of so-called "linear dodecyl sulfate", and on the other hand from the condensation on benzene of the tetramer of proplyene, giving a mixture of mainly ramified alkylaromatics, "tetrapropylbenzene".

### *3.2. Application to mixtures of alkylaromatics used as bases of sulfonation during the preparation of industrial surfactants*

The electropherograms of these two products are shown in Fig. 6. Unfortunately, there is no fine resolution of either of these two complex

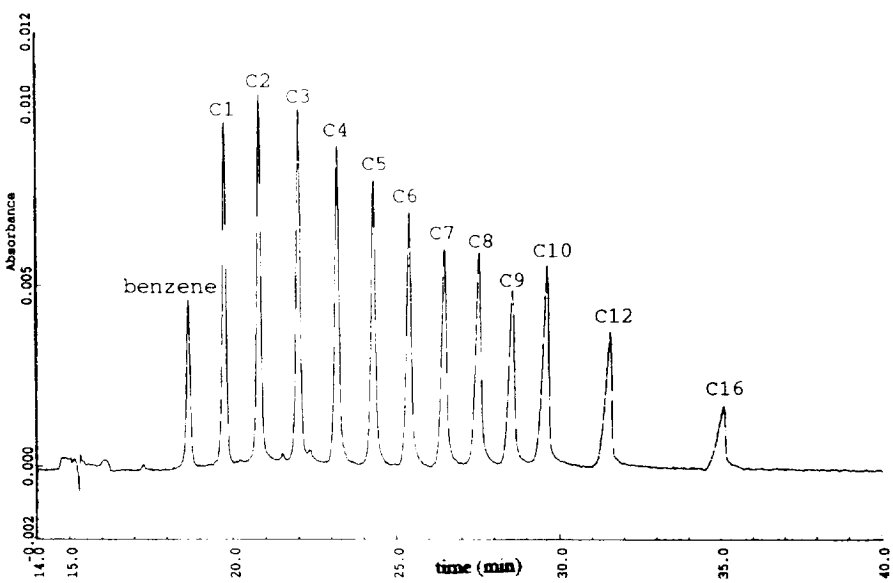


Fig. 5. Analysis of a mixture of model alkylbenzenes by capillary electrophoresis under the optimal conditions: electrolyte, 5 m*M* $NaH_2PO_4$–2.5 m*M* $Na_2B_4O_7 \cdot 10H_2O$ buffer (pH 9); [SDS], 50 m*M*; [2-propanol], 40% (v/v); temperature, 30°C; applied voltage, 30 kV; hydrodynamic injection, 1 s; detection at 214 nm.

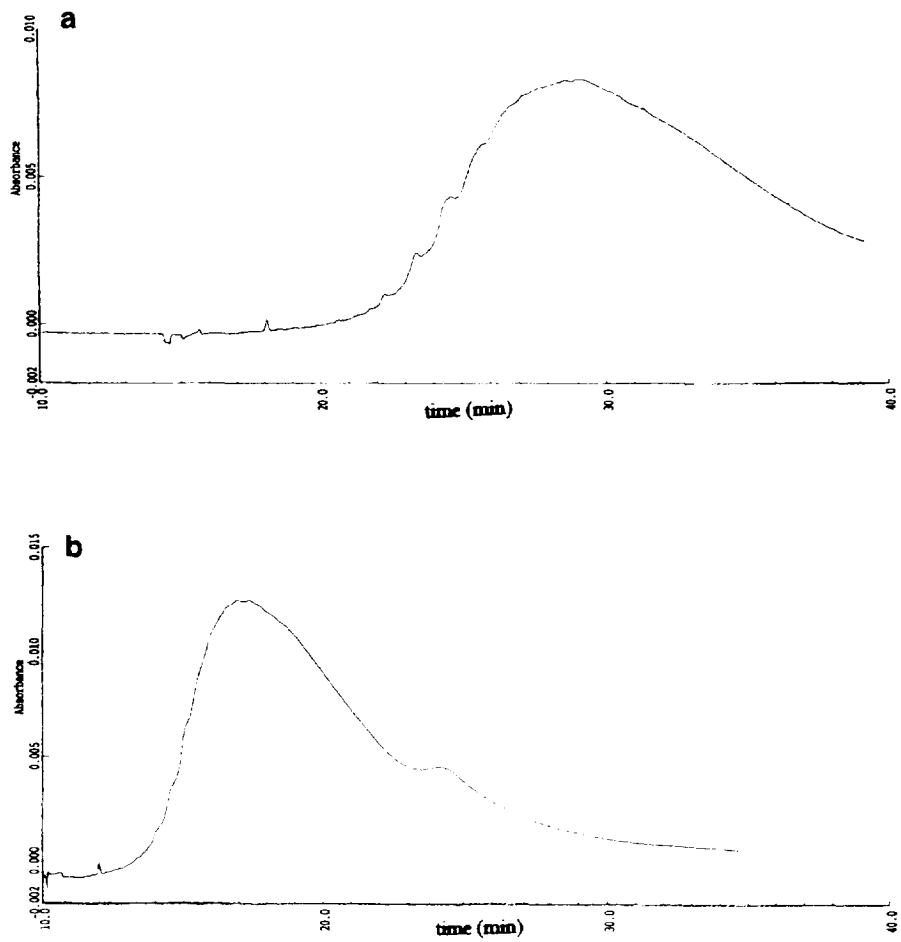


Fig. 6. Analysis by capillary electrophoresis of the bases of sulfonation used in the preparation of industrial anionic surfactants. Operating conditions as in Fig. 5. (a) Linear dodecylbenzene; (b) tetrapropylbenzene.

mixtures, and the electropherograms appear as broad and badly resolved peaks. However, it must be noted that the two mixtures of industrial alkylaromatics have very different electrophoretic behaviours under the operating conditions used. The components of tetrapropylbenzene, which are essentially ramified compounds, show migration times shorter than those of the linear dodecylbenzene components. These different behaviours result from a difference in interaction between these complex mixtures components and the SDS of the pseudo-stationary phase. The different interactions come from the lower hydrophobicity of ramified alkylbenzenes.

Considering this partial setback and the fact that increasing the amount of SDS in the mobile phase results in improved resolution, we performed the analysis of these two industrial bases of sulfonation with electrophoretic systems characterized by a higher concentration of SDS than previously (i.e., 50 m*M*), the other parameters remaining constant. Some resolution is also obtained both with linear dodecylbenzene and tetrapropylbenzene when the SDS concentration reaches 75 m*M*. This improvement in resolution is obtained to the detriment of analysis time, which increases with increasing volume of the pseudo-stationary phase.

In order to improve the resolution in time units, we tried increasing temperature of the electrophoretic medium from 30 to 40°C. As predicted by the theory, at this higher temperature the total analysis time is again acceptable, even with high SDS concentrations. This is due to the decrease in viscosity of the mobile phase, which causes an increase in the electroosmotic flow velocity.

However, a 100 m*M* concentration of SDS in the electrophoretic medium is required to obtain a satisfactory analysis of these two industrial bases of sulfonation. The corresponding electropherograms are reported in Fig. 7. In order to allow comparison of the electrophoretic behaviours, we also reported in Fig. 7 the elution range of the model alkylbenzenes under the same operating conditions.

These series of analyses indicated the following. (i) As would be expected, because of the synthesis processes used, the linear dodecylbenzene and tetrapropylbenzene are in fact complex mixtures. (ii) These two bases of sulfonation are characterized by relatively broad distributions. Effectively, the components of the linear dodecylbenzene elute at migration times extend-

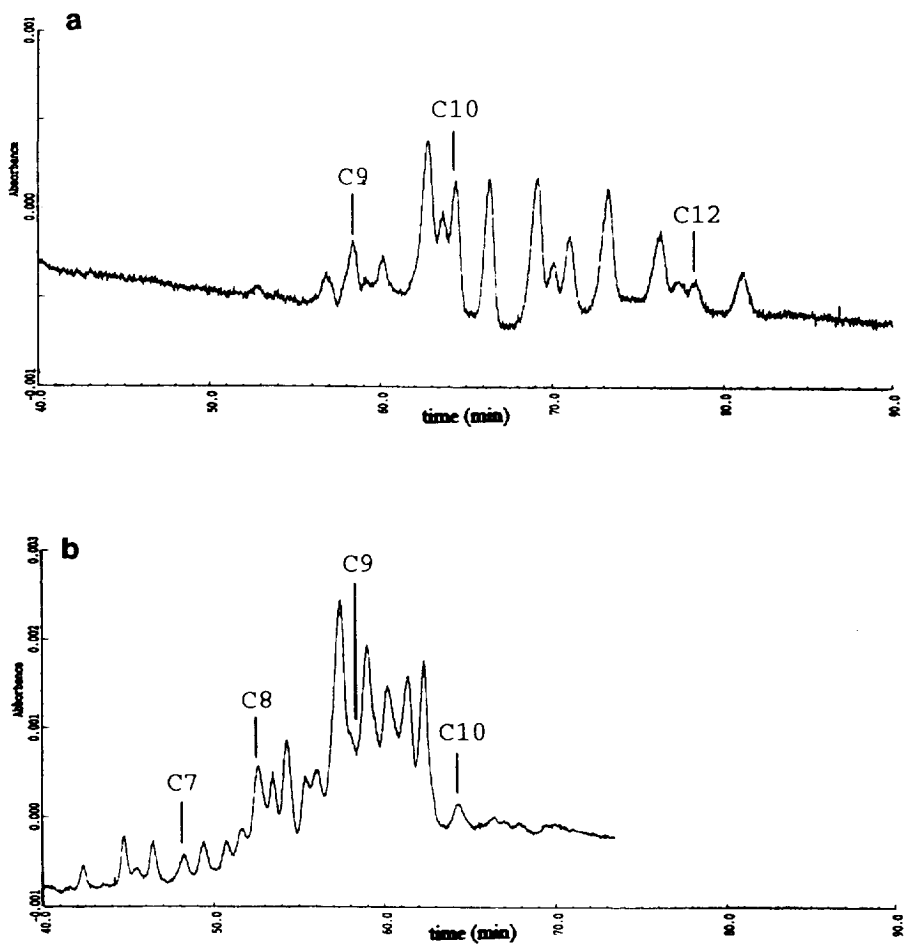


Fig. 7. Analysis by capillary electrophoresis of the bases of sulfonation used in the preparation of industrial anionic surfactants. Operating conditions: electrolyte, 5 m*M* $NaH_2PO_4$–2.5 m*M* $Na_2B_4O_7 \cdot 10H_2O$ buffer (pH 9); [SDS], 100 m*M*; [2-propanol] 40% (v/v); temperature, 40°C; applied voltage, 30 kV; hydrodynamic injection, 1 s; detection at 214 nm. (a) Linear dodecylbenzene; (b) tetrapropylbenzene.

ing respectively from those of *n*-octylbenzene and *n*-tridecylbenzene, whereas those of the tetrapropylbenzene elute between the migration times of *n*-hexylbenzene and *n*-undecylbenzene. This result justifies the designation "linear dodecylbenzene" attributed by the producer to the sulfonation base resulting from the condention of benzene on an industrial $\alpha$-olefin centred on $C_{12}$. In contrast, we cannot provide such a direct justification for the "tetrapropylbenzene", as this is mainly constituted by a mixture of ramified alkylbenzenes, in contrast of the mixture of model alkylbenzenes which are all linear. (iii) The apparent electrophoretic mobilities of the components of the tetrapropylbenzene are lower than those observed with the linear dodecylbenzene. This result emphasizes again that the tetrapropylbenzene is essentially ramified. Effectively, for an identical number of carbons in the alkyl chain, hydrophobic interactions are weaker for a ramified chain than a linear chain and therefore the components of the industrial sulfonation base must have lower electrophoretic mobilities if they are more ramified. (iv) It must be emphasized that these structural hypotheses, established from the electrophoretic behaviour of the two sulfonation bases, were perfectly confirmed by their analysis using a combination of capillary gas chromatography and mass spectrometry. This method showed that the linear dodecylbenzene is composed of alkylbenzenes with side-chains from 10 to 13 carbons, each possessing positional isomers, and the tetrapropylbenzene is essentially a mixture of ramified alkylbenzenes.

As the complexity of the anionic surfactants that we intended to study seems to result mainly from the great diversity of the alkyl side-chains, we decided to analyse then directly under conditions similar to those selected during the study of their sulfonation bases, that is, in the presence of high concentrations of SDS and of organic co-solvent.

### 3.3. Analysis of industrial anionic surfactants

Three anionic surfactants commercialized by WITCO were examined: TRS 10-80, Sulframine AcB and Sulfo TPB.

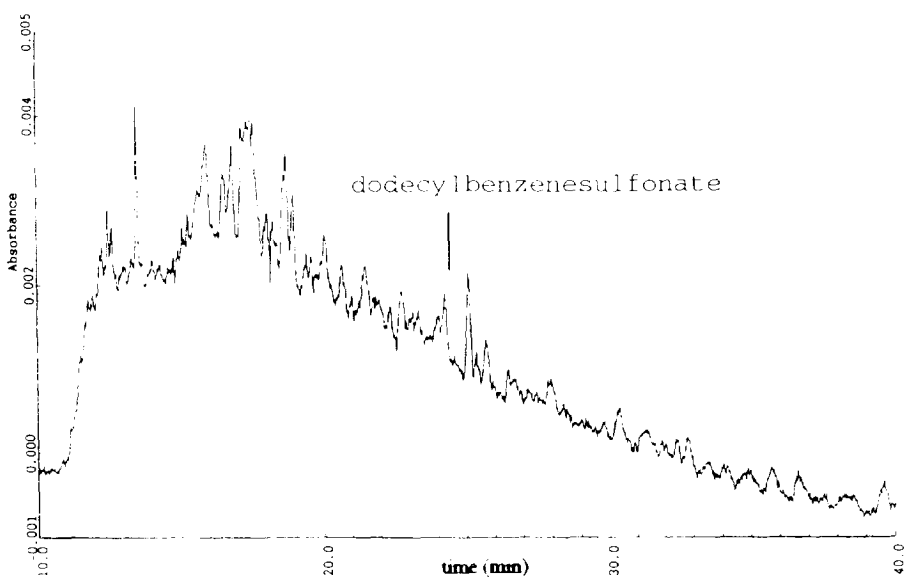


Fig. 8. Analysis of the anionic surfactant WITCO TRS 10-80 by capillary electrophoresis. Operating conditions: electrolyte, 6.25 m*M* borate–boric acid buffer, adjusted at pH 9; [SDS], 50 m*M*; [$CH_3CN$], 30% (v/v); temperature, 30°C; applied voltage, 30 kV; hydrodynamic injection, 1 s; detection at 214 nm.

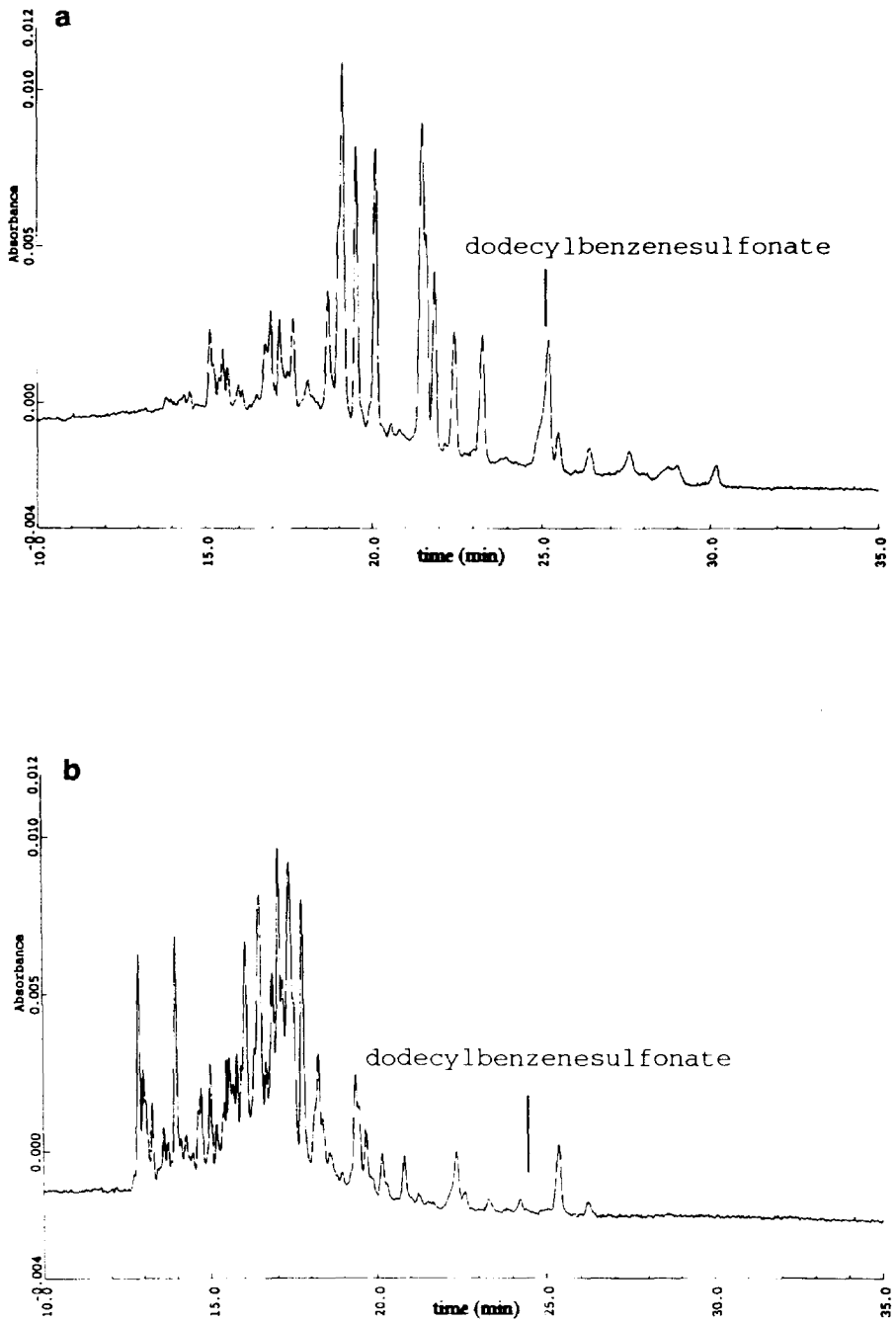


Fig. 9. Analysis of industrial anionic surfactants. Operating conditions as in Fig. 8. (a) WITCO Sulframine AcB; (b) WITCO Sulfo TPB.

*Analysis of WITCO TRS 10-80*

Considering the results obtained during the above study of the sulfonation bases, we decided to reconsider the analysis of TRS 10-80 WITCO with the following initial operating conditions: 6.25 m*M* borate–boric acid buffer (pH 9), 50 m*M* of SDS, temperature 30°C and a concentration of acetonitrile fixed in 5% steps.

As the amount of SDS was already large, we began this optimization by studying the influence on the resolution of substantial additions of acetonitrile because the amount of co-solvent in the mobile phase seemed to be, at a high SDS concentration, the other major parameter.

With the other operating parameters constant, we show in Fig. 8 the analysis of WITCO TRS 10-80 in the presence of a mobile phase containing 30% of acetonitrile. The results show that a large amount of acetonitrile, coupled with a moderate concentration of SDS, allows for the first time a relatively good separation of this complex matrix, better than the best results described previously [21], obtained using high-performance ion-exchange chromatography.

The selectivity of the electrophoretic system appears sufficient to obtain an acceptable resolution. However, this technique is still limited to the level of identification. Because of the large number of compounds separated, identification using spiking seems impossible. It appears essential, in order to complete the analysis of this complex mixture, to replace the classical UV detection with a more selective method allowing on-line identification.

After this positive result, we analysed under the same electrophoretic conditions the industrial anionic surfactants resulting from the sulfonation of alkylbenzenes obtained by condensation on benzene of either $\alpha$-olefins centred around $C_{12}$ ("linear dodecylbenzene") or tetramers of propylene ("tetrapropylbenzene"), as described above.

*Analysis of WITCO Sulframine AcB*

This anionic surfactant results from the sulfonation of linear dodecylbenzene. The electropherogram corresponding to the analysis of this mixture, under the conditions previously optimized with WITCO TRS 10-80, is shown in Fig. 9a.

As could be expected, because of the synthesis process used to prepare this product, it has a simpler matrix than WITCO TRS 10-80. However, in spite of this lesser complexity, identification by spiking is still difficult as few model molecules of this type are commercially available, a large number of syntheses would be required. The electrophoretic system developed appears to be efficient and relatively selective and allows one to separate many of the components of Sulframine AcB, particularly constitutional isomers of each homologous alkylbenzene with chain lengths of $C_{10}$–$C_{13}$.

*Analysis of WITCO Sulfo TPB*

This last surfactant results from the sulfonation of the tetrapropylbenzene base. The electropherogram corresponding to its analysis, under conditions previously optimized for WITCO TRS 10-80, is shown in Fig. 9b.

Comparison with the electropherogram obtained for Sulframine AcB (Fig. 9a) shows a greater complexity of Sulfo TPB, resulting in a poorer resolution. It appears also that apparent mobilities of the Sulfo TPB components are lower than those of the Sulframine AcB components, as evidenced by the comparison of the elution ranges of these two mixtures with the elution time of a standard compound (dodecylbenzenesulfonate, Fig. 9a and b). Therefore, sulfonated compounds possessing ramified alkyl side-chains have an electrophoretic behaviour clearly different from those of sulfonated compounds with linear chains. As in the case of alkylbenzenes, used as bases of sulfonation for the preparation of these two surfactants, this different electrophoretic behaviour results from the difference in hydrophobic interactions with SDS, which are weaker if the compound considered has a more ramified alkyl chain.

## 4. Conclusions

HPCE appears to be a particularly suitable technique for the resolution of complex mixtures

of surfactant molecules. Owing to the use of large amounts of an organic co-solvent, it was possible, for the first time, to resolve a matrix as complex as WITCO TRS 10-80.

Under operating conditions rather unusual in capillary electrophoresis, we analysed, with the same efficiency, surfactant formulations (WITCO Sulframine AcB and Sulfo TPB) and their bases of sulfonation (linear dodecylbenzene and tetrapropylbenzene). This broadens the application range of this technique from highly hydrophobic molecules to ionic molecules.

## References


[1] J.D. Knight and R. House, *J. Am. Oil Chem. Soc.*, 36 (1959) 195.
[2] E.A. Sitzkorn and A.B. Carel, *J. Am. Oil Chem. Soc.*, 40 (1963) 57.
[3] S. Lee and N.A. Puttnam, *J. Am. Oil Chem. Soc.*, 44 (1967) 158.
[4] H.Y. Lew, *J. Am. Oil Chem. Soc.*, 14 (1972) 665.
[5] S. Nishi, *Buseki-Kuyaku*, 14 (1965) 917.
[6] S. Watanabe, M. Nukiyama., F. Takagi, K. Tida and Y. Wada, *Shokuhin Eiseigaku Zasshi*, 16 (1975) 212.
[7] M. Imaida, T. Suminoto, M. Yada, M. Yoshida, K. Koyama and N. Kunita, *Shokmhin Eiseigaku Zasshi*, 16 (1975) 218.
[8] S. Matsutani, T. Shige and T. Nayai, *Yukagaku*, 28 (1979) 847.
[9] T.H. Lidicoet and L.H. Smithson, *J. Am. Oil Chem. Soc.*, 42 (1965) 1097.
[10] H.Y. Lew, *J. Am. Oil Chem. Soc.*, 44 (1967) 359.
[11] R. Dengi, *Tenside Deterg.* 10 (1973) 59.
[12] A. Nake, K. Tsuji and M. Yamanaka, *Anal. Chem.*, 52 (1980) 2275.
[13] A. Marcomini and W. Giger, *Anal. Chem.*, 59 (1987) 1709.
[14] M.A. Castles, B.L. Moore and S.R. Ward, *Anal. Chem.*, 61 (1989) 2534.
[15] A. Marcomini, S. Capri and W. Giger, *J. Chromatogr.*, 403 (1987) 243.
[16] A. Di Corcia, M. Marchetti, R. Samperi and A. Marcomini, *Anal. Chem.*, 63 (1991) 1179.
[17] A. Nakae and K. Kunihiro, *J. Chromatogr.*, 152 (1971) 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. Slater, *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] S. Chen and D. Pietrzyk, presented at the *17th International Symposium on Column Liquid Chromatography*, Hamburg, 9–14 May 1994, poster.
[21] F.E. Suffridge and D.L. Taggart, *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.
[22] P.L. Desbène, C. Rony, B. Desmazières and J.C. Jacquier, *J. Chromatogr.*, 608 (1992) 375.
[23] C. Tribet, R. Gaboriaud and P. Gareil, *J. Chromatogr.*, 609 (1992) 381.
[24] J. Romano, P. Jandik, W. Jones and P. Jackson, *J. Chromatogr.*, 546 (1991) 411.
[25] S. Terabe, *Micellar Electrokinetic Chromatography*, Beckman Instruments, Fullerton, CA, 1992.
[26] J. Vindevogel and P. Sandra, *Introduction to Micellar Electrokinetic Chromatography*, Hüthig, Heidelberg, 1992.
[27] C. Schwer and E. Kenndler, *Anal. Chem.*, 63 (1991) 1801.
[28] J. Bullock, *J. Chromatogr.*, 645 (1993) 169.
[29] P.L. Desbène and J.C. Jacquier, *J. Chromatogr.*, in preparation.
[30] Y. Walbroehl and J.W. Jorgenson, *Anal. Chem.*, 58 (1986) 479.
[31] H.T. Rasmussen and H.M. McNair, *J. Chromatogr.*, 516 (1990) 223.
[32] J. Vindevogel and P. Sandra, *Anal. Chem.*, 63 (1991) 1530.