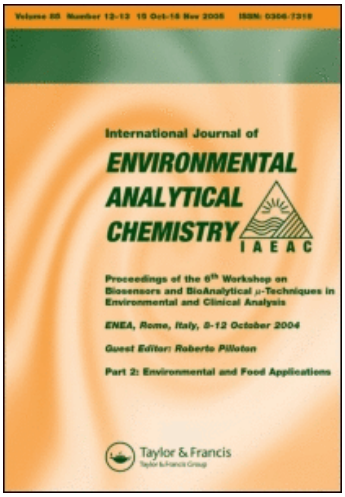

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An Ion-Pair Extraction Detector for the Liquid-Chromatographic Determination of Anionic Surfactants

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A sensitive method for the analysis of different classes of anionic surfactants based on alkyl (ether), alkylphenol (ether) and alkylbenzene formulations by means of high-performance liquid chromatography (HPLC) is described. A solvent-segmented post-column ion-pair extraction system is used to detect surfactants containing sulphate, sulphonate or sulphosuccinate as the anionic group.

HPLC is carried out with silica SI-60 as the stationary phase and mixtures of trichloromethane and ethanol containing a crown ether as the mobile phase. The column effluent is mixed with an aqueous acidic solution of the fluorogenic acridinium cation. The ion pairs formed between the anionic compounds and acridinium (Acr) are extracted into the organic phase, which then is separated from the aqueous phase and monitored fluorimetrically.

At optimum flow-rate conditions the contribution to peak broadening due to the extraction system, measured as half peak width at half height, is about 50 μl. The detection limits are at the low ng-nevel for plug injection, and from 10 to 400 ng in analysis by HPLC.

KEY WORDS: Commercial anionic surfactants, normal-phase HPLC, solvent-segmented post-column extraction detector, fluorogenic ion pairs.

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‡On transfer of work, July 1st, 1978—March 1st, 1979, from the Food Directorate, Health Protection Branch, Ottawa, Canada.

INTRODUCTION

Mixtures of anionic surface-active agents are widely employed in surfactant formulations. For the classification of the surfactants with different anionic groups various separation methods are applied, such as ion-exchange,[1] electrophoresis[2] and extraction.[3,4] A further refinement of the analysis—i.e., the separation of alkyl homologues within a class—can be realized with other chromatographic methods such as gas,[4–8] column liquid,[9–15] paper[9–15] and thin-layer[1,2,18] chromatography.

The alkyl homologues of anionic surfactants can be analyzed by gas chromatography after derivatization or degradation to the alkyl constituents.[4–8] HPLC has proved to be successful for the separation of linear alkylbenzenesulphonates[9–12] and linear or cyclic condensed phosphates[13] without pretreatment of the samples. In order to detect surfactants which do not contain a chromophoric group use is made of colour reactions in paper[16,17] and thin-layer[1,2,18] chromatography, while in HPLC a refractive-index detector is often used.[12–14] However, the sensitivity of this type of detector is rather low. Polarography with a dropping-mercury electrode has shown to be a more sensitive and selective method to detect all kinds of surfactants in aqueous solution.[14,15]

Recently, post-column reaction detectors based on the extraction of fluorescent ion pairs have been introduced for on-line detection in HPLC.[19,20] In the present paper we report on the application of this detector to normal-phase HPLC for the separation of various types of anionic surfactants present in commercial formulations and water samples.

EXPERIMENTAL

Apparatus

The HPLC equipment consisted of a reciprocating membrane pump (Orlita DMP 1515, Giessen, G.F.R.), a flow-through manometer as damping device, a high-pressure sampling valve (Valco CV-6-UHPa, Houston, Texas, U.S.A.) with a 20- and a 100-μl loop, and a stainless steel column (length, 250 mm; I.D., 3 mm).

As is shown schematically in Figure 1, the eluate from the HPLC system was monitored fluorimetrically after reaction with a fluorescent agent using a solvent-segmentation system that has been described before.[19,20] A tube pump (Gilson minipuls 2, Middleton, U.S.A.) was used to deliver the fluorescent ion pairing agent as well as to control the flow passing through the fluorimetric detector (Fluorichrom, Varian, Palo Alto, Calif., U.S.A.). Excitation and emission maxima of the extracted fluorescent ion pairs were at 360 and 470 nm, respectively. The detector output

was followed by a linear potentiometric recorder (Servogor RE 542, Goerz, Vienna, Austria).

The column was thermostatted by means of a water bath (Haake FT, Karlsruhe, G.F.R.) at temperatures of 23 and 50°C. All feed lines were constructed from stainless steel 316 tubes and Swagelok zero-dead-volume couplings.

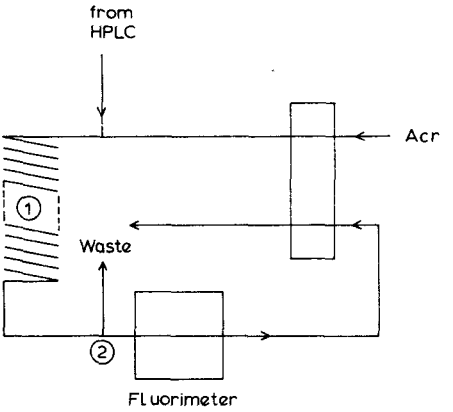


FIGURE 1 Post-column ion-pair extraction detector. 1, Extraction coil (glass, 10 turns, length 25 cm, I.D. 1.0 mm, Technicon); 2, phase separator (glass, Technicon, modified with PTFE tubes).[20] Flow-rates: HPLC (trichloromethane) 0.5–1.0 ml/min; Acr ($5 \cdot 10^{-5}$ M acridinium chloride in aqueous 0.5 M H_3PO_4) 0.5–1.0 ml/min; through fluorimeter (organic phase) 0.4 ml/min.

Materials

Silica SI-60 (Merck, Darmstadt, G.F.R.), ground and classified to a particle size range of 9–10 μm by means of an air classifier (Alpine MZR, Augsburg, G.F.R.) was used as column packing material for HPLC.

Sodium alkanesulphonates were obtained from Eastman (Rochester, N.Y., U.S.A.) and Aldrich (Beerse, Belgium) for C_1-C_7 and C_8-C_{18} alkyl chains, respectively. 1, 4, 7, 10, 13, 16-Hexaoxacyclo-octadecane (18-crown-6) was obtained from Aldrich. Acridinium chloride was obtained from Merck-Schuchardt (München, G.F.R.).

The following commercial anionic surfactants were obtained from Servo (Delden, The Netherlands): Serdet DCK 30 (C_{12}-C_{14} alkylethersulphate, 3 Mol EO), Serdet DNK 4/30 (nonylphenolethersulphate, 4 Mol EO), Serdet DM (C_{10}-C_{14} alkylbenzenesulphonate), Servoxyl VPAZ 100 (C_{12}-C_{14} alkylphosphate). Aerosol MA (dihexylsulphosuccinate) and Aerosol OT (dioctylsulphosuccinate) were obtained from Cyanamid (Rotterdam, The Netherlands). Genapol ZRO (C_{12}-C_{14} alkylethersulphate, 3 Mol EO)

and Derminollicker FNS (C_{12}-C_{22} alkylsulphonate) were obtained from Hoechst (Amsterdam, The Netherlands).

In all experiments doubly distilled water was used. All other chemicals were of analytical-reagent grade.

Procedures

The HPLC column was packed by a balanced-slurry technique.[21] The column was washed with acetone and conditioned with the mobile phase (each 100 column volumes). The mobile phase was prepared by dissolving a weighed amount of 18-crown-6 and sodium pentanesulphonate in ethanol and dilution to the appropriate eluent composition with trichloromethane. The eluent was ultrasonicated to remove air.

In order to prepare a stock solution of $5 \cdot 10^{-4}$ M acridinium chloride, 11.0 mg Acr was dissolved in 2 ml ethanol and diluted to 100 ml with 0.5 M aqueous phosphoric acid. The stock solution was kept in the dark and diluted daily to obtain a working solution ($5 \cdot 10^{-5}$ M Acr in 0.5 M H_3PO_4), which was ultrasonicated to remove air.

The alkane sulphonates were dissolved in ethanol and the solutions diluted to the appropriate eluent composition. The commercial surfactants were dissolved in the eluent and filtered over PTFE wool before injection.

RESULTS AND DISCUSSION

Optimization of the phase composition

For the separation of anionic surfactants into different classes—i.e., surfactants with the same acidic group—use was made of normal-phase chromatography. SI-60 silica was chosen as the adsorbent and mixtures of trichloromethane and ethanol containing an acid or a complexing agent, as the mobile phase.

The anionic surfactants were detected by means of an on-line post-column ion-pair extraction system and fluorimetric detection (*cf.* Figure 1). An acidic aqueous solution, containing a fluorogenic cation is mixed with the eluate from the HPLC column via a tee-piece. The surfactant anions in the organic phase (mobile phase in HPLC; carrier stream in continuous-flow analysis) and the pairing cation in the aqueous phase (reagent stream) form ion pairs at the interface of the immiscible organic and aqueous segments according to:

$$(MRX)_{org} + (BHA)_{aq} \leftrightarrows \{(BH)^+(RX)^-\}_{org} + (M^+)_{aq} + (A^-)_{aq} \qquad (1)$$

where MRX = surfactant salt, BHA = amine salt, M^+ and A^- = counter ions. The ion pairs $\{(BH)^+(RX)^-\}$ dissolve in the organic phase, which is

separated from the aqueous stream in a phase separator and monitored fluorimetrically.

For the extraction of anionic surfactants as ion pairs into an organic phase, methylene blue has been applied successfully for many years.[3,4,22] However, in this study the use of the fluorogenic acridinium cation was preferred. An about ten-fold lower detection limit could be obtained with this pairing ion as compared to methylene blue.

When optimizing the separation and detection one has to deal with three aspects: (i) keeping the background, caused by the extraction of Acr salts in the absence of surfactants as small as possible; (ii) obtaining the largest possible extraction efficiency of Acr-surfactant ion pairs; (iii) adjusting the retention and the selectivity on the column. These aspects are related to each other in an unfavourable way.[19,20] Therefore the number of degrees of freedom is limited and in practice one has to find a compromise between the desired detection limit and the separation efficiency.

The retention of the anionic surfactants, but not the selectivity, on the silica column could be adjusted by the addition of ethanol to the mobile phase. Moreover, it was found that the presence of acids and salts—e.g., phosphoric acid, formic acid, potassium acetate and sodium pentanesulphonate—decreased the retention and improved the peak shape of the surfactants. However, the background signal and the extraction efficiency depended strongly on the type and concentration of the modifier added to the mobile phase. For instance, trichloroacetate, perchlorate and, in high concentrations, chloride were found to cause interferences. These anions form an ion pair with Acr which is extracted into the organic phase and so causes a high background signal. When increasing the proportion of ethanol in the mobile phase, the capacity ratios of the surfactants decreased by a factor of 5 in going from 5 to 15% (v/v) ethanol in trichloromethane. Moreover, the extraction efficiency increased but, unfortunately, so did the background signal.

With respect to the detection system favourable conditions (i.e., detection limits of many of the surfactants investigated at the ng level) can be realized when using an organic phase consisting of trichloromethane and maximally 15% (v/v) ethanol containing $3 \cdot 10^{-3}$ M phosphoric acid and an aqueous phase containing $5 \cdot 10^{-5}$ M Acr and 0.5 M phosphoric acid. However, with this organic phase the surfactants were strongly retained in HPLC. Besides, the results were not reproducible and stable columns could not be obtained. Although such mixtures of trichloromethane, ethanol and phosphoric acid thus are not suitable for chromatographic analysis, one should realise that they may well be very useful for continuous-flow analysis.

In order to decrease the retention and to improve the peak shapes use was made of complexation by means of a crown ether (18-crown-6), as was recently done by Brugman *et al.*[23] for the separation of aromatic sulphonic acids. The retention of the anionic compounds can be adjusted by varying the concentration of the crown ether and its incorporated salt. After separation the surfactant is extracted as an ion pair with Acr according to

$$\{(CM)^+(RX)^-\}_{org} + (BHA)_{aq} \leftrightarrows \{(BH)^+(RX)^-\}_{org} + (CMA)_{org} \qquad (2)$$

where C = crown ether and M^+ = incorporated cation. As the crown ether acts as a competitor with Acr, its concentration in the mobile phase is restricted by the concentration of Acr in the aqueous phase. With $5 \cdot 10^{-5}$ M Acr in 0.5 M phosphoric acid, the maximum concentration of 18-crown-6, which does not adversely influence the detection limit of the surfactants, was found to be 1.10^{-4} M. The addition of 18-crown-6 to the mobile phase not only affects the retention, but also improves the peak shapes.

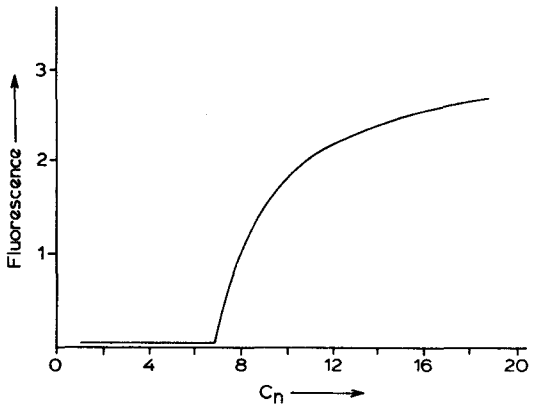


FIGURE 2 Dependence of the fluorescence on the carbon number of alkylsulphonates, determined by means of batch extraction of their ion pairs with Acr. Conditions: 10^{-5} M alkylsulphonate + 10^{-5} M Acr in 1.0 M H_3PO_4 extracted with an equal volume of trichloromethane.

From batch studies it was apparent that the Acr ion pairs of the lower alkylsulphonates are not extracted into trichloromethane (Figure 2). These compounds can therefore be used as incorporated salt for the crown ether.

Figure 3 shows the change of the detector response upon addition of the Acr reagent stream and subsequent plug injection of several surfactants for a number of mobile-phase compositions. The step in the

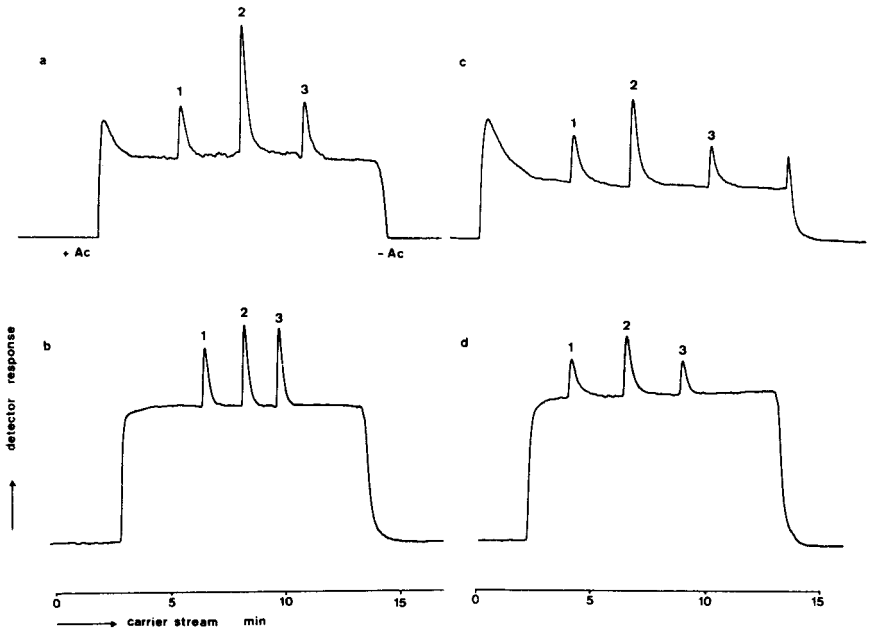


FIGURE 3 Effect of the carrier-stream composition on the response of the extraction detection determined by 20-μl plug injection of 100 ng C_{12} alkylsulphonate (1), 100 ng C_{12} alkylsulphate (2) and 100 ng C_6 dialkylsulphosuccinate (3). Carrier stream: trichloromethane-ethanol (9:1, v/v) containing: (a) 10^{-4} M 18-crown-6, $1.5 \cdot 10^{-4}$ M sodium pentanesulphonate; (b) 10^{-4} M 18-crown-6, $1.5 \cdot 10^{-4}$ M potassium acetate; (c) $1.5 \cdot 10^{-4}$ M sodium pentanesulphonate; (d) no additions. Excitation filter, 360 nm; emission filter, 470 nm. Temperature, 23°C. Flow-rates: carrier stream, 0.5 ml/min; reagent stream ($5 \cdot 10^{-5}$ M Acr in 0.5 M H_3PO_4), 0.5 ml/min; through fluorimeter, 0.4 ml/min.

detector response occurs as a result of the extraction of part of the Acr, as the phosphate salt, into the organic phase. It is obvious that the detector sensitivity increases upon addition of 18-crown-6 to the mobile phase. Besides, the background signal is seen to decrease when sodium pentanesulphonate is used instead of potassium acetate as the incorporated salt. Even in the absence of the crown ether, the presence of sodium pentanesulphonate decreases the background signal, while it also improves the peak shapes in HPLC.

Increasing the column temperature to 50°C significantly improved the column efficiency, but did not appreciably influence the retention of the surfactants or the selectivity of the system.

In all further experiments the anionic surfactants were analyzed using an organic phase consisting of 10% (v/v) ethanol in trichloromethane

containing $1 \cdot 10^{-4}$ M 18-crown-6 and $1.5 \cdot 10^{-4}$ M sodium pentanesulphonate and an aqueous phase containing $5 \cdot 10^{-5}$ M Acr and 0.5 M phosphoric acid.

Characteristics of the extraction detector

The peak broadening caused by the post-column extraction detector including the contribution of the injector and the fluorimetric detector was measured at different flow-rate combinations of the organic and aqueous phase, while the flow through the fluorimeter was kept constant. Figure 4

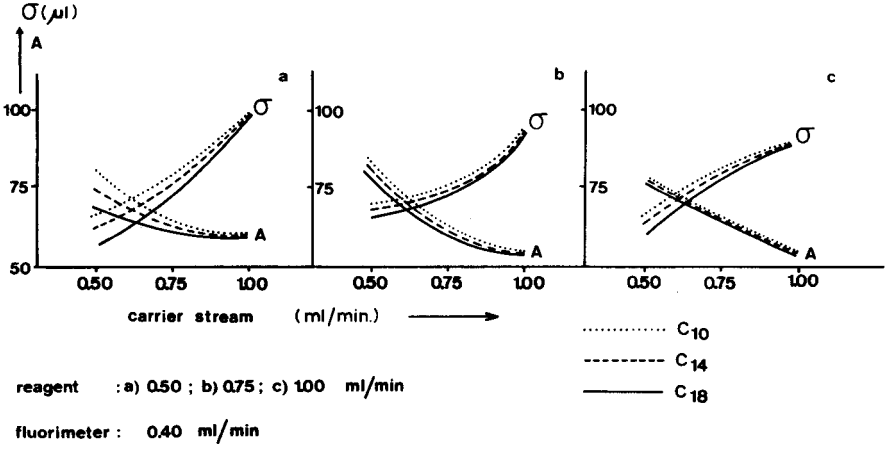


FIGURE 4 Influence of the flow-rate on peak broadening, σ, and peak area, A, for plug injection of 100 ng C_{10}, C_{14} and C_{18} alkylsulphonate directly into the extraction detector. Peak broadening (in μl) for the extraction detector including the contribution of the injector (20 μl) and the detector (22.5 μl) measured as half peak width at half height. Peak area in arbitrary units. Carrier stream: trichloromethane-ethanol (9:1, v/v) containing 10^{-4} M 18-crown-6 and $1.5 \cdot 10^{-4}$ M sodium pentanesulphonate; reagent stream: $5 \cdot 10^{-5}$ M Acr in 0.5 M H_3PO_4.

shows the dependence of the peak broadening, σ, and the peak area, A, on the alkyl chain length for a 20-μl plug injection of a solution of 5-μg/ml C_{10}, C_{14} and C_{18} alkylsulphonate. The peak broadening caused by the injector (20 μl) and the detector cell (22.5 μl) was determined by direct injection of anthracene and was found to be 30 μl. From this value and from the values given in Figure 4, the peak broadening caused by the extraction coil and the phase separator, σ_{extr}, can be calculated according to the relationship

$$\sigma^2 = \sigma^2_{extr} + \sigma^2_{inj+det} \qquad (3)$$

in which σ is measured as half peak width at half height. Minimum values (at low carrier-stream flow-rates) of σ_{extr} are of the order of 50–60 μl.

A decrease in peak area was found with increasing alkyl chain length of the sulphonate. This can probably be attributed to a disproportionate increase of the formation constants of the complexes $\{(BH)^+(RX)^-\}_{org}$ and $\{(CH)^+(RX)^-\}_{org}$ with increasing chain length. As a consequence, a decrease of the ratio between both formation constants may occur, resulting in somewhat better extraction efficiency in the order $C_{10} > C_{14} > C_{18}$.

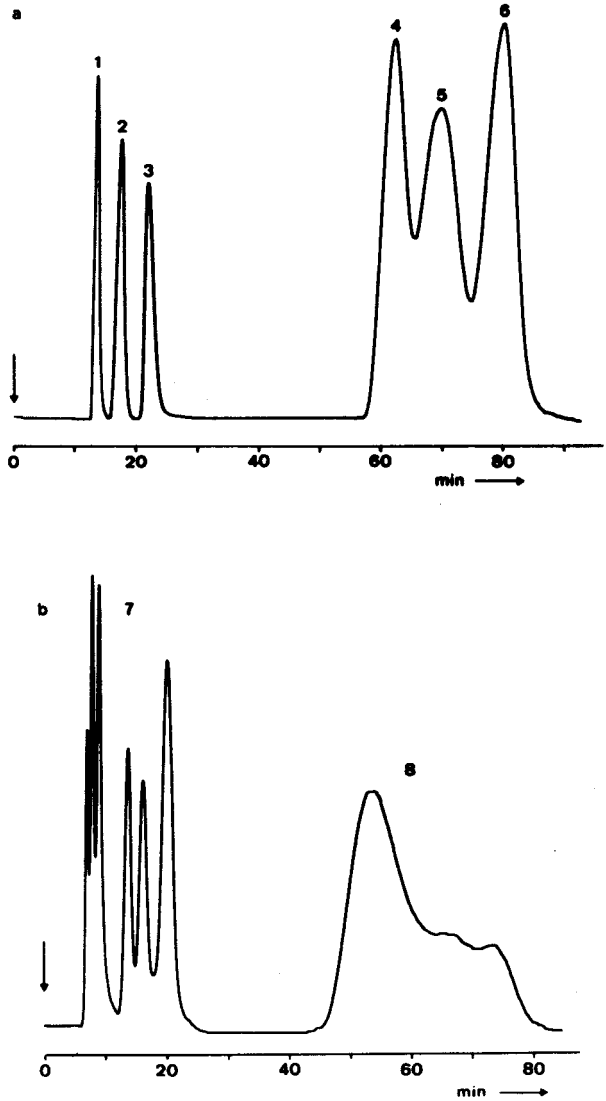
The linearity of the response of the extraction detector was determined by 20-μl plug injection of solutions of C_{10}-C_{18} alkylsulphonates. From peak-height measurements it was found that the detection system was linear over a concentration range of 3 orders of magnitude (1–1000 ng injected).

The detection limit, defined as three times the standard deviation of the noise, for the extraction detector system without the HPLC column was determined to be 1 ng for dodecanesulphate and 2 ng for both dodecanesulphonate and dihexylsulphosuccinate at a flow-rate combination of 0.5:0.5:0.4 ml/min for carrier stream: reagent stream: flow through fluorimeter (conditions as in Figure 4a). For surfactants with a phosphate group, however, a significant higher detection limit (about 1 μg for $C_{12} - C_{14}$ phosphates) was found.

Applications

The applicability of the selected phase system and the extraction detector to the analysis of surfactants is demonstrated in Figure 5. The separation of a test mixture of C_8 and C_6 dialkylsulphosuccinates, C_{12} alkylsulphate and C_{10}, C_{14} and C_{18} alkylsulphonates is shown in Figure 5a. Figure 5b illustrates the separation of some commercial surfactant mixtures. The various peaks of the alkylethersulphate sample are due to constituents with a different number of ethyleneoxide (EO) groups attached to the C_{12} and C_{14} alkyl chains. The chromatogram of another alkylethersulphate, Genapol ZRO, showed the same peak pattern as did Serdet DCK 30. The analysis of a mixture of benzylic and phenolic surfactants is shown in Figure 5c.

From a comparison of the various chromatograms one can read that the present phase system is suitable for the separation of different classes of anionic surfactants, such as alkyl (ether) sulphates from alkylbenzene- and alkylsulphonates. Due to the high detection limit of alkyl (ether) phosphates, the analysis is not disturbed by their presence in surfactant mixtures.



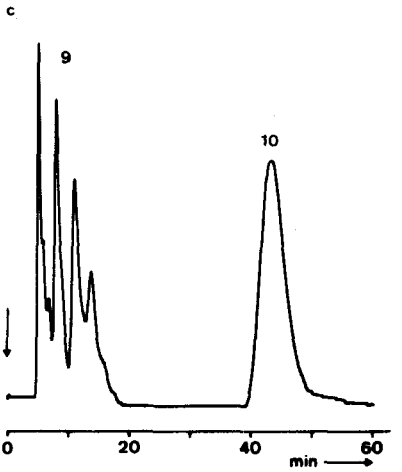


FIGURE 5 Separation of surfactants and commercial surfactant mixtures using 18-crown-6 as complexing agent in HPLC. Eluent: trichloromethane-ethanol (9:1, v/v) containing 10^{-4} M 18-crown-6 and $1.5 \cdot 10^{-4}$ sodium pentanesulphonate. Injection volume, 100 µl. Temperature, 50°C. Flow-rates: HPLC, 0.8 ml/min; reagent stream, 0.8 ml/min; through fluorimeter, 0.6 ml/min.

FIGURE 5a (1) 0.8 µg dioctylsulphosuccinate; (2) 1 µg dihexylsulphosuccinate; (3) 1 µg C_{12} alkylsulphate; (4) 8 µg C_{18} alkylsulphonate; (5) 8 µg C_{14} alkylsulphonate; (6) 10 µg C_{10} alkylsulphonate. Fig. 5b: (7) 25 µg Serdet DCK 30; (8) 40 µg Derminollicker FNS. Fig. 5c: (9) 70 µg Serdet DNK 4/30; (10) 6 µg Serdet DM.

In the present chromatographic system the separation efficiency was found to be less favourable than could be expected from the results of Brugman *et al.*[23] This must be attributed to the nature of the surfactants. In analyses of these compounds by means of HPLC the detection limits—which were dependent on the values of the capacity ratios—ranged from 10 to 400 ng. For strongly retained compounds the detection limit could be improved by using an eluent containing 15% (v/v) ethanol.

With respect to the analysis of anionic surfactants in water samples some preliminary results can be reported. Firstly, the use of 18-crown-6 as complexing agent to carry out batch extractions of anionic surfactants into trichloromethane was investigated. The organic extract was analyzed using the HPLC system described above. Recoveries were found to be low and to depend strongly on the alkyl chain length of the surfactants (about 10, 20 and 40% recovery for C_{10}, C_{14} and C_{18} alkylsulphonates, respectively). More promising results—i.e., higher recoveries and less dependence of recovery on chain length—were obtained using the conventional methylene blue extraction method.[3] Direct injection into the

HPLC system after addition of the appropriate amount of 18-crown-6 to the extracts was found to be allowed: the presence of methylene blue does not disturb the chromatographic analysis.

Secondly, trace enrichment of anionic surfactants from water samples using a pre-column[24] filled with LiChrosorb RP-18 was found to be feasible. The percentage recoveries are satisfactory and the pre-column can be washed out completely with a small volume of the organic phase containing 18-crown-6.

CONCLUSIONS

Normal-phase HPLC on silica, using trichloromethane-ethanol mixtures containing a crown ether as complexing agent as the mobile phase is very useful for the separation of different classes of anionic surfactants. In combination with a post-column extraction detector based on ion pairing, the quantitative determination of anionic surfactants, whether or not containing a chromophoric group can be carried out. The presence of a crown ether (18-crown-6) in the mobile phase improves significantly the stability and performance of the column and the detection system.

The sensitivity of the extraction detector, determined by plug injection of several types of sulphur-containing surfactants, is found to be at the ng level. This favours its potentiality in finger-print techniques for the analysis of anionic surfactants in waste water.

The results obtained so far indicate that the separation of the homologues within a class of anionic surfactants cannot be realized with normal-phase adsorption chromatography. In this respect reversed-phase chromatography with the ion-pairing reagent dissolved in the mobile phase, combined with a post-column extraction system may offer better perspectives.

Future research will be devoted to a more systematic study of the methylene blue extraction and trace-enrichment principle. Besides, the applicability of the present separation system for the analysis of anionic, cationic and nonionic surfactants will be studied. The detection of these compounds should be realized by changing the nature of the ion-pairing reagent in the aqueous stream.

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