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ANALYSIS OF α-OLEFINSULPHONATES BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

The separation and determination of the various components of α-olefinsulphonates (*i.e.*, alkenesulphonates, hydroxyalkanesulphonates and disulphonates) were carried out by reversed-phase high-performance liquid chromatography with methanol–water as eluent to which nitric acid at low concentration is added. The main peaks were identified by means of laboratory standards. The linear relationship between log k' and carbon number in homologous series is examined. Quantitation, made possible by the use of a moving-wire flame ionization detector, is applied to commercial α-olefinsulphonates produced either from single-cut olefins or from C_{14}–C_{16} mixtures.

INTRODUCTION

α-Olefinsulphonates (AOS) are widely employed not only for heavy-duty and household detergents (laundry powder) but also for toiletry liquids, owing to their excellent compatibility with other surfactants and alkaline builders and their mild effect on the environment and human beings. Moreover, the ready availability and low cost of α-olefins suggest that, in the near future, AOS could become one of the main anionic surfactants for household cleaning products[1].

In contrast to the sulphonation (or sulphation) of feedstocks such as alkylbenzenes, alcohols or alcohol ethoxylates, the manufacture of AOS involves a more complex process yielding mixtures of alkenesulphonates, hydroxyalkanesulphonates and disulphonates, with several positional isomers in each family, and requires closer control of the sulphonation conditions. Variations of the operating parameters have a significant effect on the physicochemical properties of AOS. A quick, reliable method for the determination of AOS components is needed.

The Wijs iodine value (respectively ozone number or quantitative hydrogenation) on the one hand and the hydroxyl value on the other hand provide information on the relative amounts of alkene- and hydroxyalkanesulphonates[2]. The determination of unsaturated active matter in AOS has been critically reviewed[3–5]. These methods do not allow the separation of isomers nor the discrimination of different carbon chain lengths. ^{1}H NMR spectroscopy can be used to determine alkenesul-

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phonates in mixtures[6]. Under normal conditions, 1-alkenesulphonate shows a signal separated from the other positional isomers[7]. Moreover, the utilization of a lanthanide shift reagent makes possible even the separation of the signals of isomeric alkenesulphonic acids and hydroxyalkanesulphonic acids as their methyl esters[8]. ^{13}C NMR spectroscopy which is not as quantitative, straightforwardly gives the *cis/trans* ratio of the main positional isomer[9]. Much work has been done on the indirect determination of unsaturated isomers by oxidative cleavage[3,4,9,10]. Column chromatography[3,11], thin-layer chromatography (TLC)[12–14], paper chromatography[15] and more recently high-performance liquid chromatography (HPLC)[16,17] have also been employed. Their common drawback lies in the difficulty in obtaining quantitative results. A rather lengthy (GLC) method involving several preliminary operations has also been proposed[18]. Reversed-phase HPLC with the addition of an ion-pairing reagent, a simple salt or even a strongly acidic modifier has been applied to other kinds of anionic surfactants, such as alkylbenzenesulphonates[19], alkanesulphonates and alkyl sulphates[20–22]. Aliphatic sulphonates have also been separated using ion chromatography[23].

The aim of this work was to determine the main components of AOS by HPLC in the simplest possible way*. Thus we carried out reversed-phase chromatographic analyses on AOS ranging from C_{12} to C_{18} (and containing possibly compounds of different chain lengths) with acidified (HNO_3) methanol–water as eluent.

EXPERIMENTAL

Reagents and materials

Liquid-phase batch sulphonations of 1-alkenes with an initial molar ratio of dioxane–sulphur trioxide/1-alkene lower than 1 were performed at 0°C in order to prepare samples of very low disulphonate content.

Some pure components of AOS or enriched samples were prepared for this study. 2-Hydroxytetradecanesulphonate was obtained by saponification of the corresponding β-sultone[27]. Several 3-hydroxyalkanesulphonates were synthesized using the saponification procedure of Tuvell *et al.*[28]. 4-Hydroxytetradecanesulphonate (mixed with the 3-hydroxy isomer) was obtained by hydrolysis of the corresponding δ-sultone. Alkenesulphonates (mixtures of positional isomers) were prepared by neutralization of sulphonated products with 50% aqueous sodium hydroxide at room temperature, filtration and purification according to Turbak and Livingston[29] when necessary.

Methanol and nitric acid, purchased from Prolabo, were used without further purification.

Apparatus and procedures

The liquid chromatograph comprised a Gilson Model 302 high-pressure pump, an Altex Model 210 injection valve, an Altex Ultrasphere 5 μm, RP 18 (ODS) column (25 cm × 10 mm I.D.), a Pye-Unicam moving-wire flame ionization detector LCM2 and a Shimadzu ICR1 recorder data processor.

* The determination of trace amounts of sultones present in AOS is beyond the scope of this work. This problem has also been solved by HPLC[24,25], as has the separation of alkenesulphonic acids and sultones formed during the sulphonation of 1-alkenes[26].

The reproducibility of the detector response was tested by nine identical, consecutive injections of 1,4-butanesultone directly into the detector: the relative standard deviation was about 5%. In order to verify the linearity of the response towards a given compound, solutions of known concentrations of 1,4-butanesultone in acetone were analyzed (four injections of each solution). A good straight line was obtained within the whole tested range: from 10^{-5} to 10^{-1} g l^{-1}. A very important feature of the detector is that its response is strictly proportional to carbon chain length, provided the volatility of the substance is low enough: this means that the solute volatility is negligible with respect to that of the solvent, and that, in all cases, its boiling point is higher than about 300°C. Flame ionization detection allows quantitative analysis without standard solutions of known compositions. On the other hand this kind of detector does not permit the application of ion-pair chromatography because any organic salt added to the mobile phase would cause severe perturbations of the baseline and loss of sensitivity.

Mobile phases were prepared by pipetting appropriate volumes of methanol and water (distilled and filtered). Thus the reported values of the eluent composition or volume fraction of methanol are always those before mixing. A few microliters of concentrated nitric acid (14.6 *M*) were added to the methanol–water mixture. The molarity of nitric acid is expressed assuming that the volume change upon mixing of methanol and water can be neglected. All mobile phases were kept under dry nitrogen during use. The total volume of mobile phase contained within the column, V_m, was determined by injecting silver nitrate and detecting its presence in the effluent as a precipitate by use of a solution of sodium chloride.

The capacity factors, k', for a given eluent were derived from the retention times, t_R, measured from the chromatograms and that of an unretained compound, t_0 (corresponding to V_m). From the values of the observed retention times, it was considered acceptable to neglect the travel time of the solutes on the moving wire between the column output and the detector: in fact the chosen speed was 10 cm sec^{-1}, and the time lag, not longer than a few seconds, is actually very short in comparison to t_0 (252 sec).

RESULTS AND DISCUSSION

We first sought the mobile phase composition which gave a satisfactory capacity factor range (roughly $1 \leqslant k' \leqslant 10$). With solvents less polar than water, such as methanol or acetonitrile, very short retention times are observed. The addition of water increases the retention, but the separations are characterized by poor efficiency and severe band asymmetry. Thus, convenient k' values can be obtained but the peaks are not sufficiently resolved to allow precise quantitation. Assuming that the leading peaks arise from mixed retention mechanisms, nitric acid at low concentration was added to the mobile phase. Fig. 1 illustrates the significant improvement in resolution for a pilot plant C_{14} AOS sample with $1.1 \cdot 10^{-3}$ *M* nitric acid added to the methanol–water eluent, as well as the effect of nitric acid on peak symmetry. The peaks corresponding to hydroxy- and alkenemonosulphonates were located using laboratory standards. Disulphonates were identified by taking into account that in reversed-phase chromatography more polar solutes are less strongly retained: so, among AOS components, disulphonates should be eluted early in these systems. This

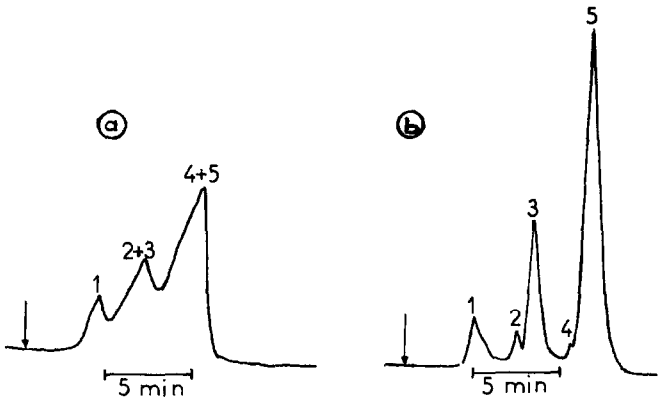

Fig. 1. Effect of HNO_3 on selectivity and peak symmetry. Column: 25 × 1 cm, Altex Ultrasphere C_{18}, 5 μm. Flow-rate: 2.5 ml/min. Sample: solution of commercial C_{14} AOS. Mobile phase: methanol–water (3:1, v/v), without HNO_3 (a), $1.1 \cdot 10^{-3}$ *M* HNO_3 added (b). Peaks: 1 = disulphonates; 2 = 4-hydroxysulphonate; 3 = 3-hydroxysulphonate; 4 = 2-hydroxysulphonate; 5 = alkenesulphonates.

assumption was confirmed by the injection of AOS samples with a very low disulphonate content. In the monosulphonate series the order of elution (hydroxysulphonates before alkenesulphonates) may also be accounted for by the more polar and hydrophilic character of the former compounds.

The effect of the mobile phase composition was investigated in a more detailed way by varying the methanol content of the eluent in the absence and in the presence of nitric acid. Fig. 2 shows the k' values of AOS components as a function of the volume fraction of methanol (before mixing). With AOS originating from single-cut olefins, separations are rather easy to perform. In the case of C_{14}–C_{16} mixtures a satisfactory k' range is obtained with a mobile phase containing 75% methanol, to which $1.1 \cdot 10^{-3}$ *M* nitric acid is added (Fig. 2b). On the other hand, by keeping the volume fraction of methanol constant (75%), longer retention times and some changes in elution order are observed at higher nitric acid concentrations (Fig. 3): for instance, k' increases in the same following sequence: C_{n+2} 4-hydroxysulphonate, C_n alkenesulphonates and C_{n+2} 3-hydroxysulphonates as shown for $n = 12$ (nitric acid $\approx 3 \cdot 10^{-3}$ *M*) and $n = 14$ (nitric acid $\approx 10^{-3}$ *M*) in Fig. 3. On the whole the selectivity seems to be better for nitric acid concentrations within the range 10^{-3}–$1.5 \cdot 10^{-3}$ *M*.

The mode of action of nitric acid is not completely understood: deactivation of free silanol groups on the stationary phase could reduce adsorption phenomena and therefore improve peak symmetry. Besides, acidification increases the solubility of sulphonates (as sulphonic acids) in organic solvents and their affinity for a C_{18}-bonded phase; thus it can influence the degree and order of retention of such compounds. The part played by nitrate ions is even less obvious: much higher concentrations of sodium nitrate have been used for similar analyses[17], whereas in $AgNO_3$-induced separations of alkanesulphonates[26], nitrate and perchlorate behave similarly, the main interaction being due to the cationic moiety[30].

Because of the greater hydrophobic interactions between the aliphatic chains

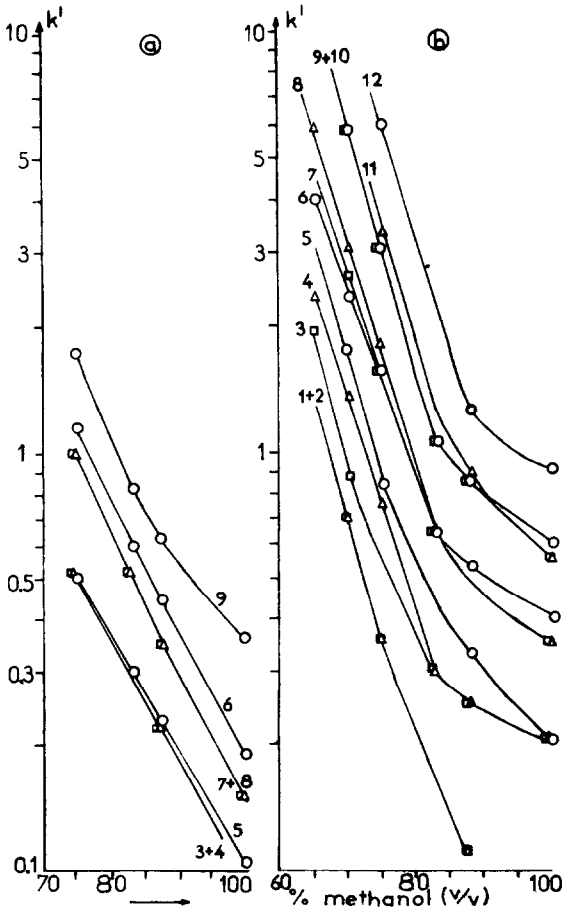

Fig. 2. Dependence of k' on the methanol content of water–methanol solvent mixtures: a, without HNO_3; b, $+1.1 \cdot 10^{-3}$ M HNO_3. Homologous compounds: ○, alkenesulphonates (A); △, 3-hydroxysulphonate (3-OH); □, 4-hydroxysulphonate (4-OH). Solutes: 1 = 4-OH C_{12}; 2 = 3-OH C_{12}; 3 = 4-OH C_{14}; 4 = 3-OH C_{14}; 5 = A C_{12}; 6 = A C_{14}; 7 = 4-OH C_{16}; 8 = 3-OH C_{16}; 9 = A C_{16}; 10 = 4-OH C_{18}; 11 = 3-OH C_{18}; 12 = A C_{18}.

and C_{18}-bonded phase, the retention increases with carbon chain length. According to the Martin rule[31], retention varies regularly in a homologous series

$$\log k' = A + Bn \tag{1}$$

where A and B are constants for a given family of compounds and a specific liquid chromatography system and n denotes the number of carbon atoms. Such a correlation has been reported for a number of homologous series of surfactants, including linear alkylbenzenesulphonates[19] and alkanesulphonates[21,22]. Linear plots of $\log k'$ *vs.* n were obtained for each series of AOS components eluted with a given mobile phase composition. Fig. 4 shows an example of such plots and Table I presents some selected values of A and B corresponding to a water–methanol eluent (3:1, v/v) modi-

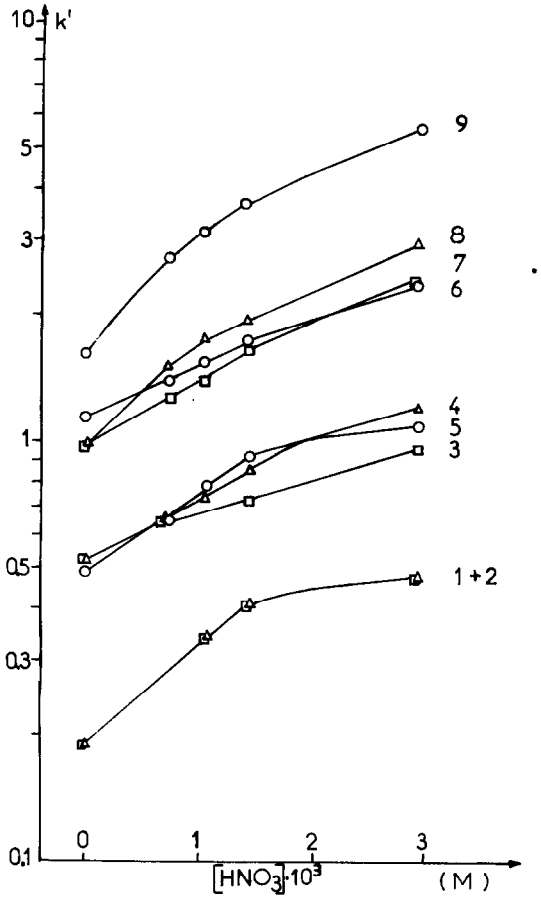

Fig. 3. Influence of HNO_3 concentration on the retention of AOS components. Mobile phase: methanol–water (3:1, v/v). Solutes as in Fig. 2.

fied by $1.1 \cdot 10^{-3}$ *M* nitric acid. We note that the *A* values are largely negative, corresponding to the high affinity of the analyzed substances for the mobile phase and the likely deactivation of almost all silanol groups by nitric acid, ruling out adsorption phenomena. As shown previously, the methylene increments are found to vary according to the functional group(s)[30,32] and above all with eluent composition[21,33] (Fig. 2b). The *B* values are of the same order as those of alkanes and carboxylic acids in the same solvent mixture[32].

The applicability of the methanol–water–nitric acid systems is demonstrated in Figs. 5 and 6, showing the separation of a pilot-plant C_{16} AOS and a commercial C_{14}–C_{16} AOS. The quantitative results pertaining to Figs. 1b, 5 and 6 are collected in Table II.

At best, analytical techniques not involving separation of AOS components only give the overall percentage of alkenesulphonates or hydroxysulphonates in mixtures containing surfactants of various molecular weights. This is why it is dif-

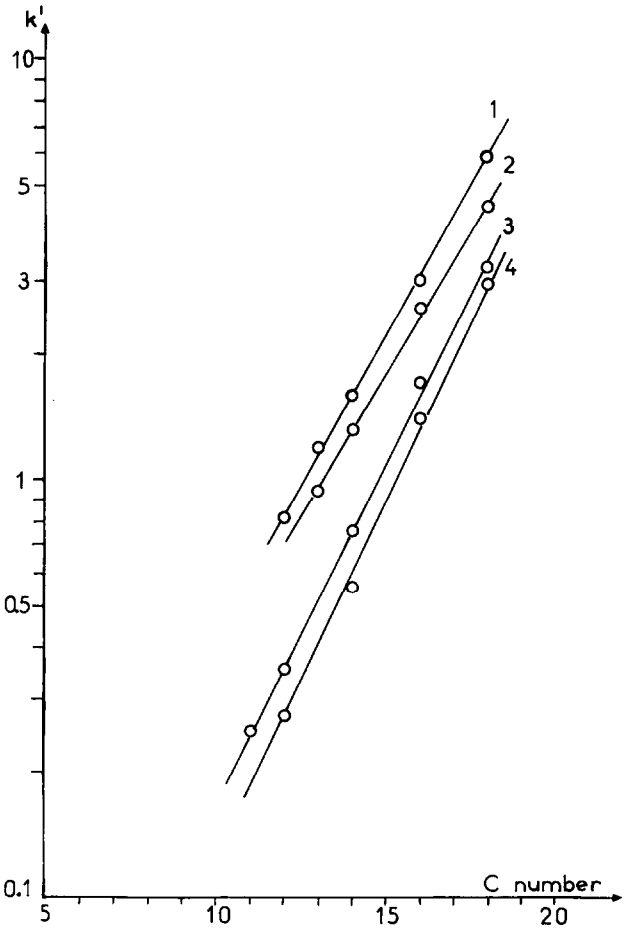

Fig. 4. Linear dependence of log k' on the number of carbon atoms for AOS components. Column and mobile phase as in Fig. 1b. Solutes: 1 = alkenesulphonates; 2 = 2-hydroxysulphonates; 3 = 3-hydroxysulphonates; 4 = 4-hydroxysulphonates.

ficult to compare the results afforded by volumetric determinations, ^{1}H NMR spectroscopy and HPLC. Keeping this limitation in mind, the iodine and hydroxyl values, as well as alkenesulphonate determination by ^{1}H NMR spectroscopy, give values consistent, within experimental error, with those obtained from HPLC separations[6].

TABLE I

PARAMETERS *A* AND *B* OF EQN. 1

Series	*A*	*B*
Sodium alkenesulphonates	−1.81	0.144
Sodium 2-hydroxysulphonates	−1.79	0.136
Sodium 3-hydroxysulphonates	−2.39	0.165
Sodium 4-hydroxysulphonates	−2.55	0.167

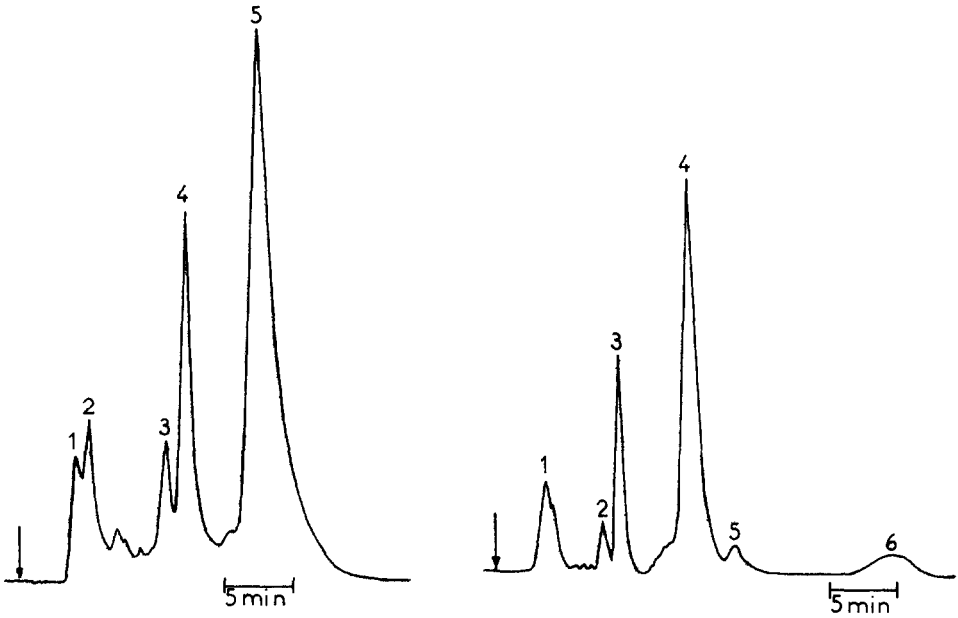

Fig. 5. Separation of a commercial C_{16} AOS sample. Experimental conditions as for Fig. 1. Peaks: 1,2 = disulphonates; 3 = 4-hydroxysulphonate; 4 = 3-hydroxysulphonate; 5 = alkenesulphonates.

Fig. 6. Separation of a commercial C_{14}–C_{16} AOS sample. Mobile phase: methanol–water (7:3, v/v) + $1.1 \cdot 10^{-3}$ *M* HNO_3. Other experimental conditions as for Fig. 1. Peaks: 1 = disulphonates; 2 = C_{14} 4-hydroxysulphonate; 3 = C_{14} 3-hydroxysulphonate; 4 = C_{14} alkenesulphonates; 5 = C_{16} 3-hydroxysulphonates; 6 = C_{16} alkenesulphonates.

TABLE II

AOS COMPOSITIONS (mol %) OBTAINED FROM THE CHROMATOGRAPHIC SEPARATIONS OF FIGS. 1b, 5 AND 6

Fig.	*Disulphonates*	*4-OH* C_{14}*	*3-OH* C_{14}	*A* C_{14}	*4-OH* C_{16}	*3-OH* C_{16}	*A* C_{16}	*2-OH and others*
1b (C_{14} AOS)	10	5	19	56				10
5 (C_{16} AOS)	10				6	19	57	8
6 (C_{14}–C_{16} AOS)	7	3	13	54	<0.5	1	17	≈5

* Nomenclature of compounds as in Fig. 2.

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