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Separation and determination of α-olefin sulphonates by salting-out chromatography

α-olefin sulphonates (AOS), one of the biologically "soft"-type detergents, have been made by sulphonation of straight-chain α-olefins (C_{15}–C_{18}) with sulphur trioxide–air followed by hydrolysis of the neutralized products[1,2]. The performance of AOS is comparable to that of a high-foaming C_{11}–C_{14} linear alkylbenzene sulphonate in both detergency and dishwashing foam[3]. These AOS are usually produced as a mixture of hydroxyalkane sulphonates ($RCH(OH)CH_2CH_2SO_3Na$) and alkene sulphonates ($RCH=CHCH_2SO_3Na$)[2].

The ratio of hydroxyalkane and alkene sulphonates in AOS depends on the conditions of preparation; a variation in this ratio may affect the performance[2,3]. It would therefore be useful to determine the ratio as a necessary first step to establishing relations between the ratio and the conditions of preparation and also between the ratio and performance.

GRIFFIN AND ALBAUGH[4] have reported the analysis of sodium α-olefin sulphonate and sodium sulphate by ion-exchange chromatography and potentiometric titrimetry. NAGAI *et al.*[5] determined mono- and di-sulphonates by thin-layer chromatography, and NAGAI *et al.*[6] analyzed AOS using the far IR spectrum. However, there are few reports on the simultaneous determination of hydroxyalkane and alkene sulphonates. RANKY AND BATTAGLINI[7] have reported analytical methods for AOS. The total active sulphonate and hydroxyalkane sulphonate were analyzed and the alkene sulphonate was calculated as the difference between them. KONISHI[8] reported an IR spectrophotometric method using carbon disulphide solution containing 5% of Amberlite LA-2 to extract AOS in aqueous solution. However, there have been no reports on the separation and determination of mixtures of hydroxyalkane and alkene sulphonates.

On the other hand, the technique of salting-out chromatography reported by SARGENT AND RIEMAN[9] has been applied to the analysis of isomeric organic sulphonic compounds[10] and anionic surface-active agents[11,12].

The present paper, one of a series of studies[11,12] on the application of this technique to the analysis of anionic surface-active agents, describes the separation and determination of hydroxyalkane and alkene sulphonates of AOS by a salting-out chromatography technique.

Experimental

Reagent and samples. Amberlite CG-50 (100–200 mesh), a weakly acidic cation-exchange resin, was used as a column substrate. Alcohol in the eluent was weighed in order to make the eluent composition precise. The standard samples of AOS (sodium 3-hydroxypentadecane sulphonate and sodium pentadecene sulphonate) were synthesized in our laboratory. Other AOS were also manufactured by our company. All reagents were of analytical reagent grade.

Procedure. The measurement of distribution coefficients and the chromatographic procedure were similar to those described earlier[11] except in the case of the composition of an eluent. Quantitative analysis was carried out by a colorimetric

method with Methylene Blue according to the JONES method as modified by LONGWELL AND MANIECE[13].

The chromatographic conditions determined finally were as follows: Resin: Amberlite CG-50 (100–200 mesh), H-form (partly Na-form); column: Sephadex (Model K25/45 Jacketed and SR25/100 Jacketed); eluent: a 30% isopropanol–0.5 *M* sodium chloride aqueous solution; column temperature: 35.0°; flow rate: 0.3 ml/min.

Results and discussion

From a preliminary examination, the sodium chloride–isopropanol system was selected as the eluent and concentration effects on the distribution coefficient of hydroxyalkane and alkene sulphonates were investigated as shown in Table I.

From the results in Table I, a 30% isopropanol–0.5 *M* sodium chloride aqueous solution was selected as eluent.

TABLE I

EFFECT OF CONCENTRATION OF ISOPROPYL ALCOHOL AND SODIUM CHLORIDE ON DISTRIBUTION COEFFICIENTS OF HYDROXYALKANE AND ALKENE SULPHONATES

Temperature: 40.0°.

Concentration of alcohol (%)	*Sodium chloride concentration* (*M*)					
	0.2		0.5		1.0	
	Hydroxyalkane sulphonate	*Alkene sulphonate*	*Hydroxyalkane sulphonate*	*Alkene sulphonate*	*Hydroxyalkane sulphonate*	*Alkene sulphonate*
25	39.3	60.9	42.2	51.1	34.2	49.6
30	14.9	19.9	20.1	35.3	15.6	21.5
35	6.5	9.1	9.2	11.1	8.8	9.8

It is thought that surface-active agents form micelles in aqueous solution and that mixed micelles are formed during the first stage of sample addition in the case of a mixed sample. Therefore, the separation of both surface-active agents will not occur if the sample passes through the column in the form of mixed micelles. It is thus necessary that the mixed micelles be dissociated to single molecules and pass through the column in that state.

In this experiment, the dissociation of AOS micelles into its single molecules was carried out with isopropanol, because AOS is well resolved in an isopropanol–water system containing a salt and the use of an alcohol with a high boiling point avoids a change in eluent composition owing to vaporization of the alcohol.

Fig. 1 shows a chromatogram obtained with standard AOS samples under the conditions mentioned above.

The first peak shows the elution of hydroxyalkane sulphonate and the second is due to alkene sulphonate. The peak resolution between them was more than unity.

Recoveries of hydroxyalkane and alkene sulphonates from the column were investigated independently, and were 98.4 and 102.3%, respectively. Known mix-

tures, prepared by mixing hydroxyalkane and alkene sulphonates in certain proportions, were analyzed and the results are shown in Table II. From Table II, it appears that the agreement between the calculated and found values is satisfactory.

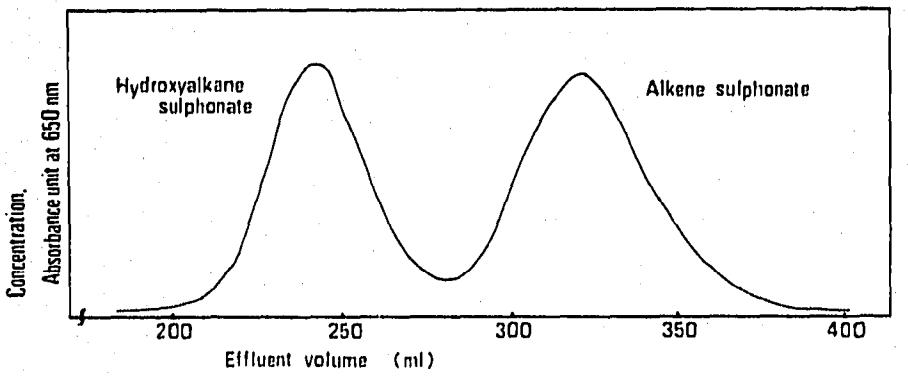

Fig. 1. Elution curve of hydroxyalkane and alkene sulphonates. Column: 25 mm I.D. × 400 mm; resin: Amberlite CG-50, 100–200 mesh; eluent: 30% isopropanol–0.5 *M* sodium chloride; sample size: hydroxyalkane sulphonate 4 mg, alkene sulphonate 4 mg; flow rate: 0.27 ml/min; temperature: 35.0°.

TABLE II

RECOVERIES OF STANDARD SAMPLES AND KNOWN MIXTURES

Sample sulphonate	*Amount taken (mg)*	*Amount found (mg)*	*Recovery (%)*
Hydroxyalkane	3.82	3.76	98.4
Alkene	3.48	3.50	102.3
Hydroxyalkane	2.68	2.70	100.7
Alkene	1.72	1.70	99.5
Hydroxyalkane	1.80	1.78	98.9
Alkene	2.78	2.82	101.4
Hydroxyalkane	3.30	3.40	103.0
Alkene	1.54	1.50	98.2
Hydroxyalkane	1.44	1.50	104.2
Alkene	3.04	3.08	101.4
Hydroxyalkane	1.92	2.00	103.2
Alkene	2.18	2.14	98.3

TABLE III

RELATIONSHIP BETWEEN ELUTION VOLUME AND LENGTH OF ALKYL GROUPS

Carbon number	*Elution volume (ml)*	
	Hydroxyalkane sulphonate	*Alkene sulphonate*
C_{14}	240	305
C_{15}	260	345
C_{16}	275	355

A single-carbon C_{15} AOS was used as a standard sample for the basic investigation. However, it is presumed that there is a difference in solubility and elution volume if the chain-length of the alkyl groups is different. Therefore, the relationship between the length of the alkyl groups of single-carbon AOS and the elution volume was studied. The results in Table III show that the elution volume increases as the chain-length of alkyl groups increases from C_{14} to C_{16} in the AOS.

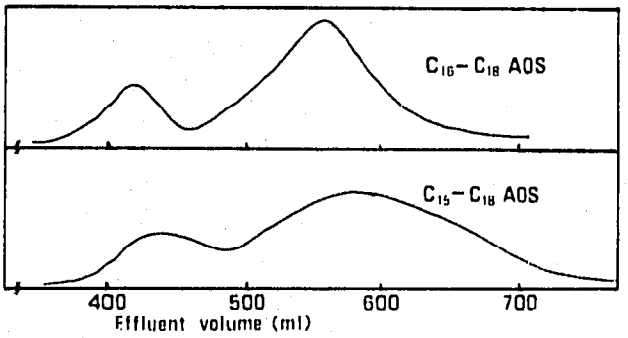

Fig. 2. Elution curves of C_{16}–C_{18} and C_{15}–C_{18} AOS. Column: 25 mm I.D. × 740 mm; resin: Amberlite CG-50; eluent: 30% isopropanol–0.5 *M* sodium chloride; temperature: 35.0°.

Fig. 2 shows chromatograms of C_{16}–C_{18} AOS and C_{15}–C_{18} AOS having a carbon-number distribution in the alkyl groups. In the case of the former, the separation of both sulphonates was satisfactory, but in the latter, separation was incomplete. However, this may be improved to a certain degree by using a longer column and a more efficient chromatographic device.

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