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Separation and determination of linear alkylbenzene sulphonates and alkylsulphates by salting-out chromatography

In the field of analysis of surface-active agents, the separation and determination of ionic surfactant mixtures is a difficult technical problem. In commercially available detergents a combination of several kinds of anionic surfactants is often found. However the separation and determination method for each anionic surfactant in these mixtures is not thoroughly established. Therefore, as a potential solution to these problems, the technique of salting-out chromatography reported by SARGENT AND RIEMAN¹ was studied.

Until now, this technique has been applied to the separation and determination of linear and branched alkylbenzene sulphonates² and hydroxyalkane and alkene sulphonates in α -olefin sulphonates³.

The present paper, one of a series²⁻⁴ of studies on the application of this technique to the analysis of anionic surface-active agent mixtures describes the separation and determination of linear alkylbenzene sulphonates (LAS) and alkylsulphates (AS) in mixtures.

Experimental

The LAS and AS were manufactured by our company. LAS was purified by a procedure similar to those given earlier². AS was purified by recrystallization from methanol. Amberlite CG-50 (100-200 mesh) was used as the column substrate and all other reagents were of analytical reagent grade.

The ion-exchange resin was washed with methanol using a Soxhlet extractor and treated with 3 *N* sodium hydroxide and 3 *N* hydrochloric acid aqueous solutions. The resin was then treated with 30 \times volumes of 3 *N* sodium chloride followed by washing with 5 \times volumes of water and drying at 105° for 5 h. The measurement of distribution coefficient, the chromatographic procedure and quantitative analysis were similar to those described earlier^{2,3} except for the composition of the eluent.

The final chromatographic conditions were as follows: column, Sephadex column (Model K25/45, jacketed); resin, Amberlite CG-50 (100-200 mesh) H-form (partially Na-form); eluent, 40% methanol-0.5 *M* sodium chloride aqueous solution; column temperature, 37.0°; flow rate, 0.3 ml/min; determination, colorimetric method with methylene blue⁵.

Results and discussion

The sodium chloride-methanol system was selected as the eluent from preliminary investigation. The effects of methanol and sodium chloride concentrations on the distribution coefficients of LAS and AS using H-form resin are shown in Table I. In the case of the purely Na-form resin, which was conditioned with 3 *N* sodium hydroxide instead of sodium chloride, the distribution coefficients of LAS and AS were much smaller than the values in Table I. This is probably because in the purely Na-form ion-exchange resin the electric repulsion forces act between the solute and the carboxyl groups of the resin, thereby reducing the distribution coefficients of LAS and AS. On the other hand, as the dissociation of H-form resin is suppressed, Van der

TABLE I

EFFECT OF CONCENTRATION OF METHANOL AND SODIUM CHLORIDE ON DISTRIBUTION COEFFICIENTS OF LINEAR ALKYL BENZENE SULPHONATES AND ALKYL SULPHATES AT 40°

| Concn. of methanol (%) | Concn. of NaCl | | | | | | | |
|------------------------|----------------|------|-------|------|-------|------|-------|-------|
| | 0.5 M | | 1.0 M | | 1.5 M | | 2.0 M | |
| | LAS | AS | LAS | AS | LAS | AS | LAS | AS |
| 30 | 98.7 | 34.8 | 187.7 | 65.7 | 257.9 | 91.3 | 269.6 | 119.9 |
| 35 | 65.5 | 24.7 | 78.0 | 39.1 | 159.5 | 52.0 | 131.4 | 83.2 |
| 40 | 34.2 | 14.6 | 70.6 | 22.8 | 121.4 | 25.7 | 185.2 | 44.8 |
| 45 | 25.2 | 7.8 | 29.5 | 11.4 | 35.3 | 14.4 | 53.0 | 24.6 |

Waals' interaction between the solute and the resin is large and the distribution coefficients are correspondingly large.

From Table I, a 40% methanol-0.5 M sodium chloride aqueous solution was selected as the eluent.

Examination on a column (I.D. 25 mm, length 100 mm) was carried out under the above mentioned eluent system at 40.0°. Although AS was eluted completely, LAS was mainly adsorbed on the resin. Thus, the elution of LAS was very difficult in comparison with AS, probably because Van der Waals' interaction between the LAS

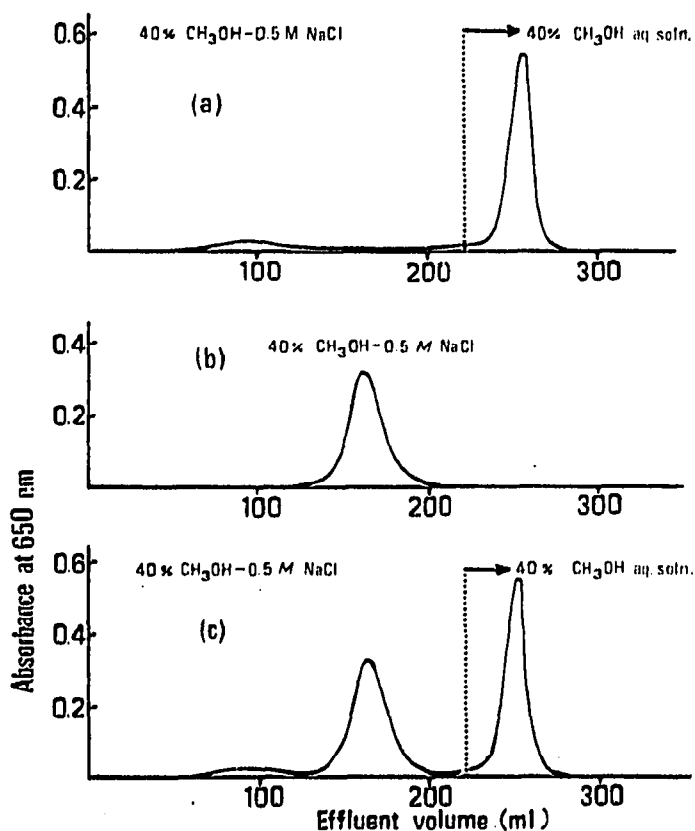


Fig. 1. Elution curves of LAS, AS and their mixtures. Column: 100 mm \times 25 mm I.D.; resin: Amberlite CG-50, 100-200 mesh; eluent: 40% CH_3OH -0.5 M NaCl; flow rate: 0.3 ml/min; temperature: 37.0°; samples: (a) LAS, 2.67 mg; (b) AS, 1.98 mg; (c) LAS, 2.67 mg, AS, 1.98 mg.

molecule and the resin skeleton is stronger, due to the presence of a benzene ring in the molecule of LAS in comparison with only alkyl groups in AS.

If the concentration of methanol in the eluent was increased, the elution volume of LAS approached that of AS and the separation of both was incomplete. By raising the column temperature the same result was obtained. Therefore, after AS was eluted, 40% aqueous methanol solution without sodium chloride was used in order to elute the LAS on the resin.

Fig. 1 shows the chromatograms obtained with LAS and AS under the final conditions mentioned above. The small peak in front of the main peak of LAS in Fig. 1b is assumed to be due to the elution of by-products or to be a peak based on low-molecular-weight LAS. This small peak is found to overlap the elution volume of AS even under conditions in which the main peak of LAS is scarcely eluted.

The recoveries of LAS and AS from the column were investigated independently and found to be 100.9 and 99.5%, respectively. In the case of analysis of a mixture, the recovery of LAS from its main peak, which appeared after the eluent composition was changed to 40% aqueous methanol solution, was 91.6%, the remainder (8.4%) overlapping with the AS fraction. Therefore, for the quantitative analysis of the mixture, an amount of LAS corresponding to 8.4% was subtracted from the amount of AS and added to that of LAS.

TABLE II

RECOVERIES OF STANDARD SAMPLES AND KNOWN MIXTURES

| Samples | Taken(mg) | Found(mg) | Recovery(%) |
|------------------|-----------|-----------|-------------|
| LAS ^a | 2.67 | 2.69 | 100.9 |
| AS ^a | 1.98 | 1.97 | 99.5 |
| LAS | 2.67 | 2.70 | 101.0 |
| AS | 1.98 | 1.96 | 99.1 |
| LAS | 2.67 | 2.69 | 100.9 |
| AS | 3.97 | 3.99 | 100.5 |
| LAS | 5.35 | 5.45 | 101.9 |
| AS | 1.98 | 1.96 | 99.0 |
| LAS | 1.78 | 1.77 | 99.7 |
| AS | 3.97 | 4.06 | 102.2 |
| LAS | 4.01 | 4.17 | 104.0 |
| AS | 0.99 | 1.01 | 101.8 |

^a Average of two determinations

Known mixtures, prepared by mixing LAS and AS in certain proportions, were analyzed and the results are shown in Table II. It appears that the agreements between calculated and determined values are satisfactory.

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