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Note

A study of the separation mechanism of ionic surfactants in salting-out chromatography

Functions of alcohol and sodium chloride in the eluent

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The technique of salting-out chromatography has been applied to the separation and determination of organic non-electrolytes[1] and dyestuff intermediates[2] since it was proposed by Sargent and Rieman[3]. It has also been developed in order to establish an analytical method for the separation and analysis of mixtures of ionic surfactants[4,5].

In general, an aqueous inorganic salt solution is used as the eluent in salting-out chromatography. However, in the analysis of surfactants, an alcohol must be added to the aqueous salt solution in order to increase the solubility of the surfactants in the eluent. Thus a ternary solvent system, water–alcohol–salt, is employed as the eluent.

The present investigation was undertaken in order to establish the functions of the alcohol and salting-out agent in the eluent in the salting-out chromatography of ionic surfactants by measuring the distribution ratio of water and alcohol in the ion-exchange resin.

It was found that the function of the alcohol in the eluent is to dissociate the mixed micelles of surfactants into single molecules and to dissolve them in the eluent. On the other hand, the function of the salting-out reagent is to render both the surfactant molecules and alcohol molecules in the eluent adsorbable on the resin. On the basis of these results, it was possible to explain the elution behaviour of ionic surfactants in salting-out chromatography.

EXPERIMENTAL

A glass filter-tube similar to that employed by Pepper *et al.*[6] was used in order to remove residual solvent held externally on the beads of swollen resin. The tube, 10 mm in diameter and 45 mm in height, was sealed at the bottom with a sintered-glass disc of porosity 2. A rubber cap was utilized in order to prevent evaporation of solvent during centrifuging. A small hole was pierced in the rubber cap so as to equalize the internal and external pressures. A centrifugal separator (Model H-301, Kokusan Ensin, Tokyo, Japan) was used to remove residual solvent outside the resin.

A Karl Fischer titrator (Model MK-A, Kyoto Electronic Manufacturing, Kyoto, Japan) was employed to determine the water content.

Amberlite CG-50 (100–200 mesh), a weakly acidic cation-exchange resin, was used as the resin. All other reagents were of analytical-reagent grade. The alcohols used were methanol, ethanol and isopropanol.

The resin was washed with methanol in order to remove impurities, converted into the H^+ form by the usual method, and dried at 105° for 1 day. The water content of the dried resin was less than 0.1%.

The measurements of the distribution ratio of water and alcohol in the resin were carried out according to the procedure described by Pepper et al.[6]. The overall precision of the determination of alcohol in the resin, obtained by difference, was less than ±2.4%.

RESULTS AND DISCUSSION

The distribution of water and alcohol in the Amberlite CG-50 (H^+) resin was measured in aqueous solutions of each alcohol of various concentrations and the results are shown in Fig. 1, in which the proportion of alcohol in the internal solution (expressed as per cent by weight) is plotted against that in the external solution. At low alcohol concentrations in the external solution (less than 60%), the proportion of alcohol in the internal solution is much higher than that in the external solution, regardless of the alcohol considered. At high alcohol concentrations, however, the proportion of alcohol in the internal solution is lower than that in the external solution. This tendency follows the order isopropanol>ethanol>methanol.

At low alcohol concentrations, it is thought that the system is stabilized when alcohol is transferred into the resin phase, as reported by Marcus and Naveh[7].
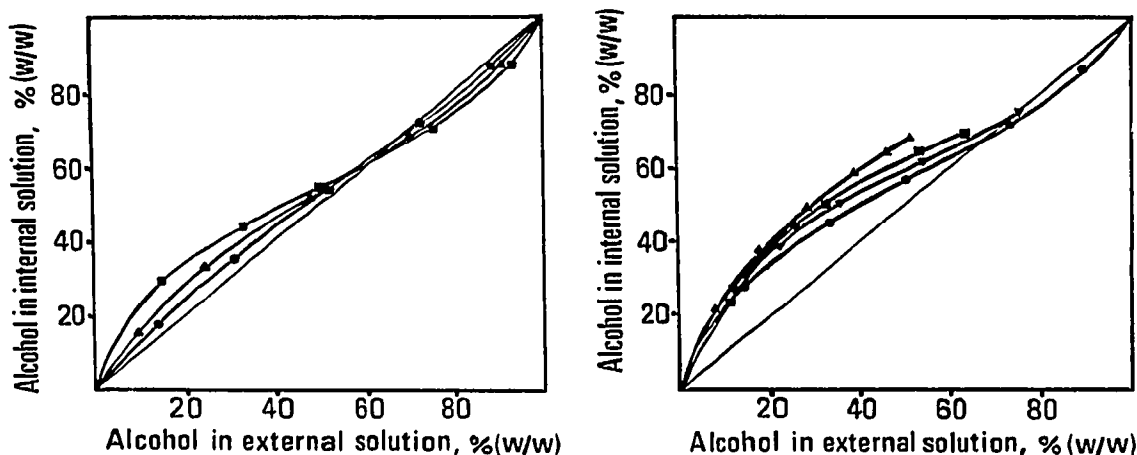

Fig. 1. Distribution of alcohols between the solution phase and the resin phase. Alcohol: ●, methanol; ▲, ethanol; ■, isopropanol.

Fig. 2. Effect of sodium chloride on the distribution of isopropanol between the solution phase and the resin phase. Sodium chloride concentration: ●, 0; ▼, 0.1; ■, 0.5; ▲, 1.0 M.

In order to clarify the function of sodium chloride in the eluent, the distribution of solvent in the H^+ form of the resin was investigated by using aqueous alcohol–sodium chloride solution as solvent. Fig. 2 shows the distribution curves obtained with isopropanol as the alcohol. The proportion of isopropanol in the internal solution increases as the concentration of sodium chloride increases. From a comparison of Fig. 2 with Fig. 1, it is apparent that sodium chloride in the eluent aids the adsorption of isopropanol molecules on to the resin.
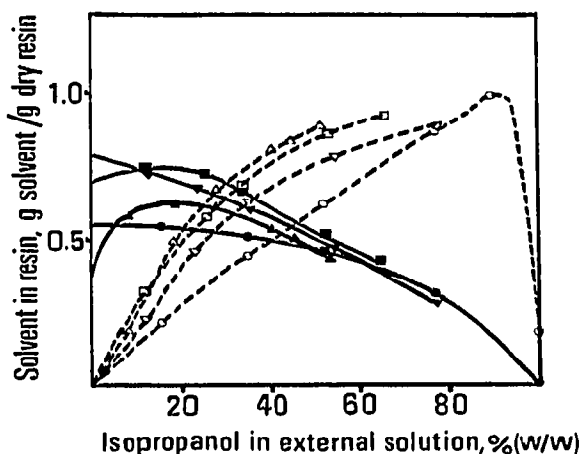

Fig. 3. Uptake of solvent by the resin in aqueous isopropanol–sodium chloride solutions of various concentrations. ———, Water; – – – –, isopropanol. Sodium chloride concentration: ●, ○, 0; ▼, ▽, 0.1; ■, □, 0.5; ▲, △, 1.0 M.

Fig. 3 shows the effects of sodium chloride on the uptake of water and isopropanol in the resin. The amount of isopropanol in the resin increases with increase in the salt concentration, and it is thought that the isopropanol molecules were adsorbed on the resin as a result of the salting-out action of sodium chloride.

In the aqueous ethanol–sodium chloride system, the effects of sodium chloride on the distribution of ethanol in the resin were smaller than those on the distribution of isopropanol. Further, in the aqueous methanol–sodium chloride system, the proportion of methanol in the internal solution did not show any remarkable change on adding sodium chloride. These results show that the shorter the hydrocarbon chain in the alcohol, the less the alcohol is subject to salting-out action and accordingly it is less adsorbed on the resin.

On the basis of these results, it seemed reasonable to assume that the function of sodium chloride is to exert a salting-out effect on alcohols. On the other hand, the function of the alcohol, as discussed above, is to decrease the effective area of the resin available for the adsorption of surfactant molecules.

In a previous paper dealing with the salting-out chromatography of surfactants, Fudano and Konishi[4] found that the elution volumes of samples increased as the salt concentration in the eluent increased, but decreased again at higher salt concentrations. These results can be explained by considering the function of the salting-out reagent clarified in the present study. When an aqueous isopropanol solution without

salt is used as an eluent, surfactant molecules dissolve in the eluent and are not ad-sorbed on the resin. By the addition of sodium chloride to the aqueous isopropanol solution, not only does the solubility of the surfactant molecules in the eluent decrease, but also both the surfactant and the alcohol molecules are "pressed" on to the resin by the salting-out effect of sodium chloride, thereby being adsorbed on the resin. At low salt concentrations, the surfactant molecules are more salted-out compared with alcohol molecules. As the amount of surfactant adsorbed on the resin increases with increase in the salt concentration, the elution volume of the surfactants consequently becomes larger. At higher salt concentrations, as the effective adsorption area for the surfactant molecules decreases owing to the high adsorption of alcohol on the resin, the adsorption of surfactants is inhibited and the elution volume decreases again.

Fudano and Konishi[8] examined the effect of methanol on micelle dissociation in the aqueous methanol–ammonium sulphate system. It can be concluded from these results that the salting-out chromatography of surfactants can be carried out only with eluents in which the surfactants are dissociated into single molecules.

Surfactants form micelles in aqueous solution and, when two types of surfac-tants are present in an aqueous solution, mixed micelles are formed. The separation of both surfactants will not occur if the sample passes through the colomn in the form of mixed micelles. It is therefore necessary for the mixed micelles to be disso-ciated into single molecules and to pass through the column in that state. This can be regarded as another function of alcohols.

CONCLUSIONS

The first function of the alcohol in eluents composed of aqueous alcohol–sodium chloride solution is to dissociate the mixed micelles of surfactants into a unimolecular state. On the other hand, the function of sodium chloride as salting-out reagent is to render not only surfactant molecules but also alcohol molecules adsorb-able on the resin by means of its salting-out action. Consequently, both surfactant and alcohol molecules compete for occupation of the effective adsorption sites of the resin, and the amounts of them adsorbed change in accordance with the concentration of sodium chloride. With increase in the salt concentration, the salting-out effect on the alcohol becomes high, thereby decreasing the effective adsorption area for sur-factants (the second function of the alcohol).

Thus, it can be concluded that ionic surfactants can be quantitatively separated into their components by salting-out chromatography in which the first and the second functions of the alcohol, and the varying solubility of surfactants in aqueous alcohol–salt solution, and also the different salting-out effects of the salt on each surfactant molecule, are utilized.

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