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The Salting-out Adsorption of Isomeric Butyl Alcohols by Macroreticular Resin

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The salting-out adsorption of isomeric butyl alcohols on Amberlite (200) type designated as the macroreticular ion-exchange resin (MR type) was studied. On the basis of the difference in the salting-out effect of isomers, the separation of the isomer mixture in a dilute aqueous solution was attempted by using an aqueous ammonium sulfate solution as an eluent and the MR resin as a stationary phase. It seems that MR resin as the stationary phase is inadequate for the salting-out chromatography of isomeric butyl alcohols.

The salting-out effect in the two-phase system has been investigated on butyl alcohol in the aqueous and the butanol phases.[1] The present paper will report the salting-out adsorption of isomeric butyl alcohols on ion-exchange resin by determining the relative solubilities in an ammonium sulfate solution. The Amberlite (200) type of cation exchange resin was used. This resin, designated as macroreticular (MR) ion-exchange resin, is entirely different from the conventional homogeneous gels and has a rigid macroporous structure similar to those of the conventional absorbents.[2,3] Whereas the specific surface area for a conventional resin is very small (0.1 m^2/g), this resin has a surface area of 54.8 m^2/g.[2] On the basis of the difference in the salting-out effect on isomers, the separation of an isomer mixture in a dilute aqueous solution was attempted by using an aqueous ammonium sulfate solution as an eluent and the MR resin as the stationary phase. The designation "Salting-out Chromatography" has been proposed for such a method of separation.[4,5] The only convenient method known to the authors for the determination of each isomer in the above mixture is that of gas chromatography. However, in this case, such a method is not applicable because of the undesirable phenomena of water tailing.

Experimental

Procedure. All the chemicals were reagent-grade and were used without further purification. The Amberlite (200) type of cation exchange resin was converted to the ammonium form by the passage of 1 M ammonium sulfate solution and was then dried at 50°C overnight. This resin has the capacity of 4.3 meq/(g of dry resin), a water content of 44.8% and a pore size of 60—300 Å. The batch adsorption was made by adding 3—4 g of MR resin to 50 ml of a 0.5% butanol solution with a 0.5—3 M ammonium sulfate solution. After this mixture had been allowed to stand at 25°C, overnight, the butyl alcohol in the aqueous solution was determined. In the case of column adsorption, the resin was packed into a column (ϕ 1.25 cm × 22.5 cm) water-jacketed and connected to a bath maintained at 25°C. Before elution, the resin was equilibrated with the eluent to be used. This was accomplished by allowing 300 ml of the eluent to pass through the column. A 0.5 mmol portion of the butyl alcohol was pipetted onto the bed. Then, the column was drained with a flow rate of 0.3 cm/min. The separation of isomers was attempted with the above-mentioned column and with a larger column of ϕ 1.7 × 70 cm. Both columns had an interstitial volume of 36%.

Analysis. The butyl alcohols were determined by oxidizing them in 50% sulfuric acid with dichromate and by measuring the reduced Cr(III) spectrophotometrically.[6] A 100 g portion of sodium dichromate was dissolved in water, and the mixture was diluted with water to 100 ml. A 5 ml portion of this solution was added to an 1000 ml solution of the concentrated sulfuric acid. At this time, the precipitate appeared, but it was redissolved on shaking. A 25 ml portion of a sample contanining 0.0025—0.01 mmol of butyl alcohol was pipetted into a 100 ml flask containing 25 ml of above oxidizing agent. Similarly, a flask was prepared by adding 25 ml of water to 25 ml of the oxidizing agent. The flask was heated in a boiling water bath for 15 min. After cooling to room temperature, the absorbance was measured at 610 mμ against the blank. Oxidizing anions such as nitrate and reducing ions such as halides interfered with this determination. Ammonium sulfate was the best eluent because of its large solubility in water and its great salting-out power.[4] Since the absorbance was slightly affected by ammonium sulfate,

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[1] Y. Kurokawa and N. Yui, *Nippon Kagaku Zasshi*, **88**, 276 (1967).

[2] K. A. Kun and H. Hisayama, *Kagaku to Kogyo*, **21**, 1465 (1968).

[3] R. Kunin, E. E. Meizner, J. A. Oline, S. A. Fisher, and N. Frisch, *Ind. Eng. Chem., Prod. Res. Develop.*, **1**, 140 (1962).

[4] W. Rieman, *J. Chem. Educ.*, **38**, 338 (1961).

[5] W. Funasaka, T. Kojima, K. Fujimura, and S. Kushida, *Bunseki Kagaku*. **15**, 835 (1966).

[6] R. Sargent and W. Rieman, *Anal. Chim. Acta*, **14**, 381 (1956).

the plot of the absorbance *vs.* the concentration of butyl alcohol was made at each concentration of ammonium sulfate. Absorbance measurements were made with a HITACHI EPU-2A-type spectrophotometer.

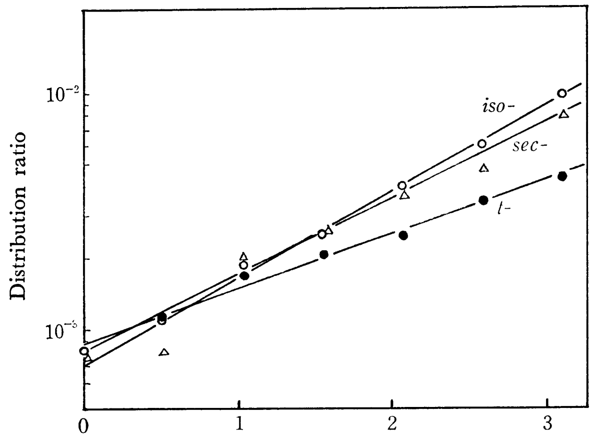

Fig. 1. Plots of log *D* *vs.* concentration of $(NH_4)_2SO_4$ for isomeric butanols with Amberlite 200.

Results and Discussion

The distribution ratio of butyl alcohol was defined as D=(the quantity of adsorption mmol/g-dry resin)/(concentration of aqueous solution mmol/l). Correction was made for the swelling and shrinking of the resin. The logarithms of these ratios are plotted against the concentration of ammonium sulfate in Fig. 1. These plots followed fairly closely this equation:

$$\log D = \log D^{\circ} + kM \qquad (1)$$

where D° is the distribution ratio in pure water, k is a salting-out coefficient, and M is the molarity of ammonium sulfate. Eq. (1) is very similar to Setshenow's equation.[1] The obtained values are represented in Table 1. D showed a rough tendency to decrease as the hydrophilic nature of the butyl alcohol increased. That is, the order of k was the same as that of the solubilities of butyl alcohols in water, (*tert*-butanol is completely miscible with water). The MR resin is observed to be much less sensitive to the nature of the solvent than conventional resin, but the results are not so much less sensitive in the literature.[3] The increase in the salt concentration of the eluent produced a greater affinity of the resin for butyl alcohol. The ionic groups on the resin would be solvated preferentially by water, and when salt was added, the resin would shrink because a part of the water was withdrawn to solvate the salt. Then, the solvated position around the ionic group on the resin could now be occupied by butyl alcohol.[7] Two kinds of solvent uptake by the resin might be considered. One might be a chemisorption as solvation around the ionic group on the resin, and the other, physisorption as fixing into the rigid macropores.[8] The adsorption of butyl alcohol on the MR resin was rather small, whereas the MR resin had a capacity as large as that of the conventional resin and had a much larger surface area. This suggests that water molecules are tightly bound to resin and may not be easily substituted by butyl alcohol molecules. Each isomeric butyl alcohol was eluted with a 3M ammonium sulfate solution. The elution graphs are shown in Fig. 2. They are very like each other. The ordinate is the absorbance of the Cr(III) formed by the reduction of dichromate by the butyl alcohol and is, therefore, proportional to the concentration of butyl alcohol in the eluent. Generally, a smaller mesh size of a resin produced a sharper elution curve, but no significant shift of the peak was observed. When the

TABLE 1. DISTRIBUTION RATIO AND SALTING-OUT COEFFICINET

		Amberlite-200		Dowex 1-X8 column	Dowex 50-X8 column
		batch	column		
$\log D^{\circ}$	iso-	−0.145		0.330	0.130
	sec-	−0.073		0.150	0.039
	t-	−0.061		−0.125	−0.130
k	iso-	0.374		0.380	0.407
	sec-	0.322		0.422	0.419
	t-	0.238		0.414	0.408
$\log D$	iso-	0.613	0.645	1.00	0.944
	sec-	0.571	0.614	0.994	0.877
	t-	0.415	0.424	0.703	0.686

Eluent of 2M $(NH_4)_2SO_4$ was used.

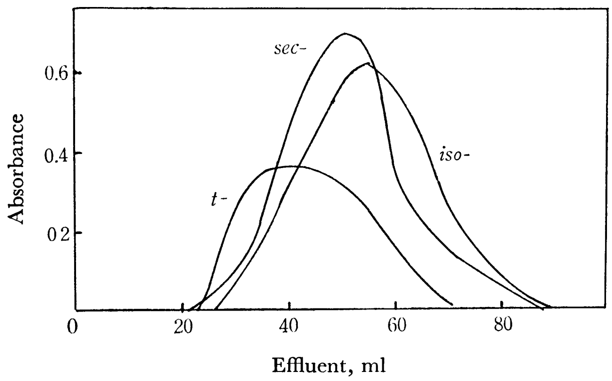

Fig. 2. Elution of isomeric butanol.
Column of ϕ 1.25×22.5 cm, 0.3 cm/min
Eluent of 2M $(NH_4)_2SO_4$

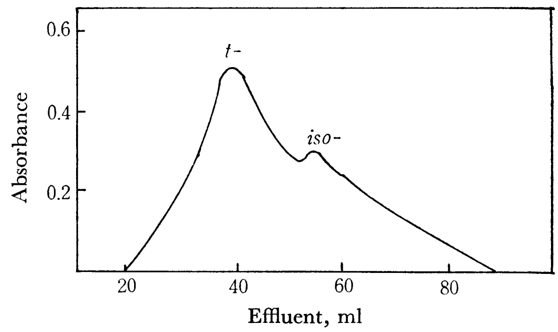

Fig. 3. Elution of isomers mixture.
Column of ϕ1.25×22.5 cm, 0.3 cm/min
Eluent of 2M $(NH_4)_2SO_4$

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7) R. Sargent and W. Rieman, *J. Phys. Chem.*, **61**, 354 (1957).

8) T. Yamabe, K. Yamagata, and M. Seno, *Nippon Kagaku Zasshi*, **89**, 151 (1968).

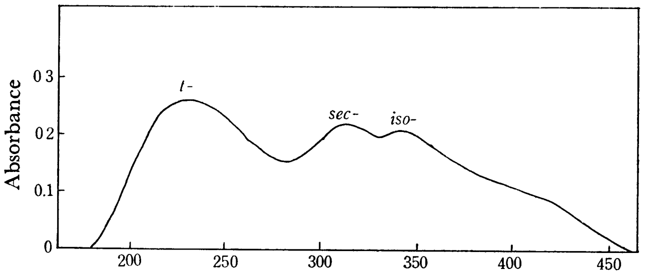

Fig. 4. Elution of isomers mixture.
Column of $\phi 1.75 \times 70.5$ cm, 0.26 cm/min
Eluent of 2M $(NH_4)_2SO_4$

quantity of butyl alcohol taken for elution was too large, the curve was wide and subject to tailing.

The distribution ratios in the column were obtained from the elution curves by using the following plate theory of chromatography:[9]

$$U = DV + V \qquad (2)$$

U is the volume of the effluent collected by adding the sample to the peak. D is the distribution ratio, and V is the interstitial volume of the column. Table 1 represents a comparison of these values for the MR resin with those for the conventional resin. The separation of isomers was attempted with two columns. The elution of the first column for a mixture of *iso*- and *tert*-butanol is shown in Fig. 3. Another elution was performed by using a column much larger than the first (Fig. 4). The curves overlapped so badly that a satisfactory separation could not be achieved. The position of the peak was estimated from Eq. 2, and the value of D was obtained from the first column. The calculated values of U for *tert*-, *sec*-, and *iso*-butyl alcohol were 23.1, 29.5, and 31.2 ml respectively. The agreement between the calculated and observed values seems reasonable, though the peaks overlap (Fig. 4). The elution required 30 hr for the completion of a run. The separation might be made more completely with a column of a higher height. It seems that the MR resin as the stationary phase is inadequate for the salting-out chromatography of isomeric butyl alcohols.

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[9] R. Sargent and W. Rieman, *J. Phys. Chem.*, **60**, 1370 (1956).