NOTES

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Synthetic Inorganic Ion-exchange Materials. XIII. The Mutual Separation of Alkali Metals with Three Different Antimonic Acids

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The present paper will describe the use in the chromatographic separation of alkali metal ions on columns of the three different antimonic acids;[1] amorphous (S_A), glassy (S_G), and crystalline (S_C). The samples were prepared as was been described in a preceding paper,[2] and then controlled

TABLE 1. DISTRIBUTION COEFFICIENTS AND SEPARATION FACTORS (α) ON THREE DIFFERENT ANTIMONIC ACIDS

Exchanger	Solution	Li		Na		K		Rb		Cs
S_A	1×10^{-3}M MNO_3	1.0×10^2		4.1×10^2		1.5×10^3		2.8×10^3		5.8×10^3
	0.1N HNO_3	6.4		27.8		123		196		226
	(α)		4.3		4.4		1.6		1.2	
	0.05M NH_4NO_3	7.7		24.8		41		41		31
	(α)		3.2		1.7		1.0		0.76	
S_G	1×10^{-3}M NMO_3	2.6×10^2		7.5×10^2		2.5×10^3		6.0×10^3		9.8×10^3
	0.1N HNO_3	10.4		37.4		167		238		318
	(α)		3.6		4.4		1.4		1.3	
	0.05M NH_4NO_3	12.5		37.5		55		44		37.3
	(α)		2.5		1.7		0.8		0.85	
		Li		K		Cs		Rb		Na
S_C	1×10^{-3}M MNO_3	7.1×10		1.76×10^4		3.5×10^4		1.3×10^5		1.0×10^6
	0.1N HNO_3	0.9		4.5×10^2		1.4×10^3		8.1×10^3		8.3×10^4
	(α)		500		3.1		5.8		10.2	
	0.05M NH_4NO_3	2.5		10.4		37.3		56.2		890
	(α)		4		3.6		1.5		15.8	
		Li		Na		K		Rb		Cs
Amberlite IR-120	1×10^{-3}M MNO_3	1.6×10^3		3.1×10^3		4.2×10^3		7.8×10^3		1.3×10^4
	0.2N HNO_3	19.5		30		64		85.5		100
	(α)		1.5		2.1		1.3		1.2	
Zirconium phosphate	1×10^{-3}M MNO_3	1.7×10^2		1.1×10^3		3.8×10^3		9.8×10^3		1.9×10^4
	0.1N HNO_3	15.0		41		140		390		910
	(α)		2.7		3.4		2.8		2.3	

Exchanger: 0.100 g ,total volume: 25.0 ml, 20±0.05°C, immersion; 24 hr.
S_A: amorphous antimonic acid, S_G: glassy antimonic acid, S_C: crystalline antimonic acid.

Distribution coefficient was calculated from the following equation;

$$K_d = \frac{A_0 - A_s}{A_s} \cdot \frac{\mathrm{m}l}{\mathrm{g}}$$

where A_0 is the concentration of alkali metal in the solution before equilibration (1×10^{-3} mol/l), A_s is the concentration in the solution after equilibration, ml is total volume of the solution in mililiters, and g is the weight of the sample in grames.

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[1] M. Abe and T. Ito, This Bulletin, **41**, 333 (1968).

[2] M. Abe and T. Ito, *ibid.*, **41**, 2366 (1968).

in a 100—200 mesh size. The column experiments were carried out with a column ($0.8\phi \times 6.0$ cm) containing 3.0, 6.4, and 3.9 g for S_A, S_G, and S_C respectively. The concentration of alkali metals was determined flame-photometrically by using a Hitachi EPU-2A with a flame apparatus, H-2, attached.

Results and Discussion

Affinity Series for Alkali Metal Ions. Table 1 gives the values of the distribution coefficients for alkali metal ions on three different antimonic acids. The K_d values on S_C are higher than those on S_A and S_G except in the case on Li^+ adsorption, and S_A gives values almost identical with those obtained on S_G. The affinity on the S_A and S_G was found to increase in the order: $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ in the acid solution, while the order was: $Li^+ < Na^+ \fallingdotseq Cs^+ < K^+ = Rb^+$ in the ammonium nitrate solution. The affinity series on the S_C may be written as $Li^+ < K^+ < Cs^+ < Rb^+ < Na^+$ in the acid solution and $Li^+ < K^+ < Rb^+ < Cs^+ < Na^+$ in the ammonium nitrate solution. The difference in selectivity is very large compared with those obtained for the sulfonic acid resins. In the acid solution, Rb^+ was more strongly adsorbed than Cs^+, with the separation factor of 5.8. Na^+ was more strongly adsorbed than any other alkali metal ions in the solutions of both nitric acid and ammonium nitrate. The separation factor in the pairs of lithium and other alkali metals may be compared favorably with those of other cation exchangers.

According to Lefebvre,[3] the inverse selectivity should prevail for alkali metals: $Na^+ < K^+ < NH_4^+ < Rb^+ < Cs^+$ on the polyantimonic acid.

When a large volume of a 0.1 N soultion of various alkali metal salts was passed through an S_C column, the uptake of alkali metals showed the values of 1.0, 2.8, 2.4, 1.4, and 1.2 meq/g for Li^+, Na^+, K^+, Rb^+, and Cs^+ respectively. In the solutions with a constant ionic strength of 0.1 M ($HNO_3 + MNO_3$), ion-exchange isotherms on the S_C gave ogee-sharp curves,[4] as is the case with rigid inorganic ion-exchangers (*e. g.*, zirconium phosphate, zeolites, and basic cancrinite). These results indicate that the selectivity coefficient varies strongly with the ionic composition and that the reversal of selectivity, which may be due to steric factors, arises from the course of conversion. The crystalline antimonic acid presents a fairly rigid lattice, for the volume change on conversion from the hydrogen form to the alkali forms is very small; accordingly, the lattice constants of various forms gave 10.30, 10.33, 10.37, 10.38, 10.40 and 10.47 Å for Na, Rb, Li, H, Cs, and K forms, without any change in the crystal system. The increased order in the lattice constant conforms to the inverse order in the affinity series for micro amounts of all the alkali metal ions except Li^+.

Separation of Alkali Metal Ions on the Columns of the Three Different Antimonic Acids. Small amounts of various alkali metal ions were adsorbed onto the column and then eluted with different eluants.

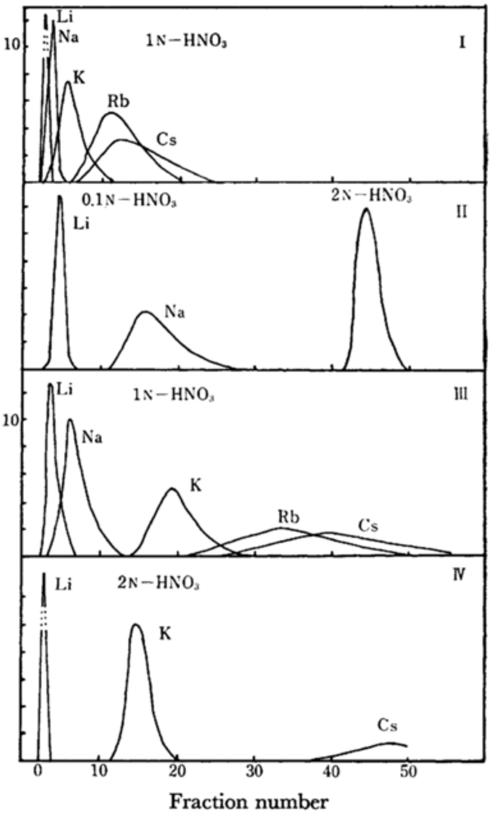

Fig. 1. The elutions of alkali metals with nitric acid of various concentrations on the three different antimonic acids.
Fraction: 5.5 m*l*, alkali metal: each 0.02 mmol, flow rate; 0.3 m*l*/min
I and II: amorphous antimonic acid, III: glassy antimonic acid, IV: crystalline antimonic acid.

Elution with Various Nitric Acid Solutions. On the S_A and S_G, all of the alkali metal ions were more easily eluted with nitric acid of a relatively dilute solution than in the case of S_C, and the elution curves were always somewhat asymmetric. Complete separation were made for Li^+, Na^+, and K^+ with an 0.1 N (S_A) or 0.2 N (S_G) and 2 N nitric acid solution. On S_C, a good separation was obtained for Li^+, K^+, and Cs^+ with a 2 N nitric acid solution, but Na^+ and Rb^+, were not eluted within 70 fractions.

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[3] J. Lefebvre and F. Gamard, *C. R. hebd. Seanc. Acad. Sci., Paris*, **260**, 6911 (1965).

[4] M. Abe and T. Ito, Preprints for The 19th Annual Meeting of The Chemical Society of Japan (April, 1966) Vol. II, p. 292.

It has been established that, on the organic ion-exchangers, the mutual separation between Rb^+ and Cs^+ is very difficult. The separation on the S_C can be made completely with a 4N nitric acid solution. The separation factor, α_{Rb}^{Cs}, calculated from the peak volume in the elution curves showed 5.6. Sodium ions were more strongly adsorbed than any other alkali metal ions and could not be eluted by a relatively concentrated nitric acid solution within the column volume shown in Fig. 2-I. Figure 2-II shows that the order of peak volume in the elution curves was $K^+ < Cs^+ < NH_4^+$ and that S_C was not for selective for ammonium and cesium ions, while there was a broader curve for cesium ions. With eluants of both nitric acid and ammonium nitrate solutions, the time required was relatively short, only about 10 hr being sufficient for a complete separation of a miligram-amount of alkali metals (Fig. 3-I).

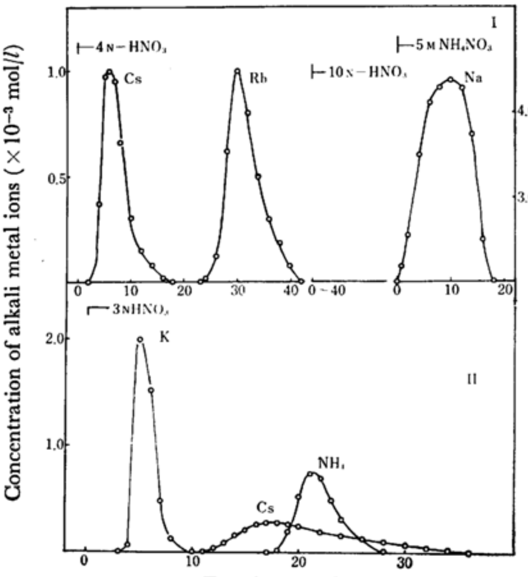

Fig. 2. The elution of alkali metals on crystalline antimonic acid

I: separation of sodium, rubidium and cesium fraction; 5.5 m*l*, Rb and Cs; each 0.04 mmol, Na; 0.1 mmol

II: elution of potassium, cesium and ammonium, ions fraction; 5.6m*l*, K, Cs and NH_4; each 0.02mmol

Flow rate: 0.3 m*l*/min.

Elutions with Various Ammonium Nitrate Solutions. On S_C, pairs of neighbouring alkali metal ions, such as Li-K, K-Rb,and Cs-Na, were easily separated in the same column length, but not the Rb-Cs pair (Fig. 3-II). On S_A and S_G, all the alkali metal ions except Li^+ were removed as a group with a 0.03M ammonium nitrate solution.

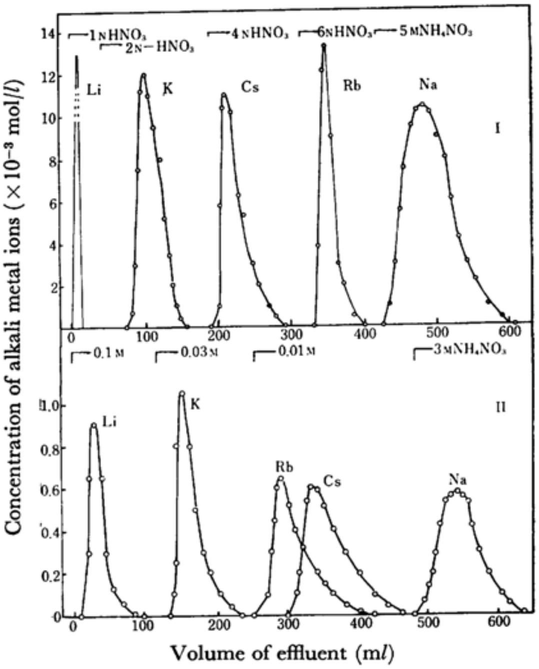

Fig. 3. The separation of alkali metal ions with nitric acid and ammonium nitrate of various concentration on the crystalline antimonic acid S_C. Flow rate: 0.6 m*l*/min.

I: with the nitric acid and ammonium nitrate solutions, Li; 0.01 mmol, Na; 0.1 mmol, K, Rb, Cs; each 0.04 mmol

II: with the ammonium nitrate solutions, Li; 0.02 mmol, Na, K, Rb, Cs; each 0.04 mmol

These results indicate the presence of antimonic acid of two types, with a different selectivity for alkali metal-ions adsorptions, a difference may be closely related to the disparity in the surface structure.[2] The S_G and S_C were favorable for column work because their lower solubilities and their suitable granular forms. The S_C was especially stable against almost all reagents, including concentrated acid and alkaline solutilons and oxidizing agents. The S_A was unsuitable, since it was relatively soluble in water and was gradually transformed into crystalline antimonic acid in a relatively concentrated acid solution.

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