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SYNTHETIC INORGANIC ION-EXCHANGE MATERIALS

XV. CHROMATOGRAPHIC SEPARATION OF ALKALI METAL IONS USING PHOSPHOANTIMONIC(V) ACID AS A CATION EXCHANGER

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SUMMARY

The use of phosphoantimonic(V) acid as a cation exchanger in the chromatographic separation of alkali metal ions has been investigated. The mutual separation of alkali metal ions (except the Li^+–Na^+ pair) was achieved by using a relatively small column (6.0 × 0.8 cm I.D.) with ammonium nitrate solution as the eluent.

INTRODUCTION

The analytical applications of synthetic inorganic ion-exchange materials have increased considerably during the last 10–15 years[1–4], and the separation of alkali metals by cation exchange has been studied extensively with both organic and inorganic ion exchangers. The selectivities for alkali metals on inorganic ion exchangers, *e.g.*, zirconium phosphate and tungstate, are generally more favourable than those on organic ion-exchange resins and the mutual separations of alkali metals have been achieved with relatively short columns[5–7].

As has been shown by several workers[8–11], the precipitate consisting of antimony pentoxide and orthophosphoric acid (so-called "phosphoantimonic(V) acid") is a strong monobasic acid that has useful adsorption properties for alkali metals even in dilute acidic solution.

Our earlier work[8,9] showed that the phosphoantimonic(V) acid (P-SbA), formed by pouring antimony pentachloride into orthophosphoric acid solution, exhibited reversible exchange behaviour with the system K^+–NH_4^+, and that the potassium ions adsorbed strongly on the column of the hydrogen form of P-SbA were not eluted with up to 28 column volumes of 3 N hydrochloric acid followed by 25 column volumes of 3 N nitric acid[9].

This paper describes the possibility of effecting separations of alkali metal ions with P-SbA using ammonium nitrate solution as the eluent.

EXPERIMENTAL

Preparation of P-SbA

P-SbA was prepared as described previously[9] and conditions favourable for the formation of glassy material were chosen. The precipitate of P-SbA was obtained by diluting a mixed solution of antimony pentachloride (50 ml) and 4 M orthophosphoric acid (100 ml) with 900 ml of demineralized water. The colloidal precipitate was kept in the mother liquid at 80° on a steam-bath for 16 h and was then filtered off. The glassy material was obtained by drying the filtered precipitate at 80°.

On subsequent immersion in water, the glassy material broke down into smaller particles as in the case of hydrous zirconium oxide and amorphous zirconium phosphate, after which it was stable on further treatment with aqueous solution. The product was washed with water until it was almost free from chloride ions. After drying in air, the sample was sieved to give the 100–200-mesh fraction.

Chemical composition of P-SbA

The glassy sample was melted with potassium nitrate in a platinum crucible and the mixture was dissolved in water. Antimony was separated as antimony sulphide by passing hydrogen sulphide into the solution. The content of antimony was determined iodimetrically after dissolving the antimony sulphide in hydrochloric acid containing a small amount of potassium chloride. Phosphate was determined gravimetrically as magnesium pyrophosphate in the usual manner using the filtrate. The water content of the air-dried sample was determined by subtracting the sum of the weights of Sb_2O_5 and P_2O_5 from the weight of the sample.

Conversion of hydrogen form into ammonium form of P-SbA

A column of dimensions 6.0 × 0.8 cm I.D., containing 3.6 g of the hydrogen form of P-SbA, was employed. The ion-exchange capacity was determined by titration of hydrogen ions eluted from the column against 0.2 M ammonium nitrate solution with methyl orange as the indicator.

Distribution coefficients

The distribution coefficients (K_d) of alkali metals were determined by shaking 0.100 g of the exchanger with 25.0 ml of a $1 \cdot 10^{-3}$ M solution of alkali metal containing various concentrations of ammonium nitrate. Equilibria were attained in 24 h. The K_d values were calculated from the equation

$$K_d = \frac{\text{Amount of metal in exchanger}}{\text{Amount of metal in solution}} \cdot \frac{\text{ml of solution}}{\text{g of exchanger}}$$

The concentrations of alkali metals were determined flame-photometrically by using a Hitachi EPU-2A instrument equipped with an H-2 flame apparatus.

Separation of alkali metals on P-SbA column

After conversion into the ammonium form, the mixed solution containing 0.02 mmole of each alkali metal was passed through the P-SbA column (6.0 × 0.8 cm I.D.). The alkali metal ions adsorbed were eluted with ammonium nitrate solution of different concentrations.

RESULT AND DISCUSSION

Preparation and composition

The glassy material is physically stable in various aqueous solutions, which is useful in column operations. A means was therefore sought of preparing the glassy product from the precipitate of P-SbA. The material prepared by the method described above is a hard, glassy gel provided that the molar ratio of orthophosphoric acid to antimony pentachloride in the starting material is greater than 1; below this value and at lower concentrations than that mentioned above a fine product was formed. The composition of P-SbA agreed well with earlier reports[8,9], viz., the ratio of phosphate to antimony (P:Sb) was 0.5. The occurrence of this limiting value in the preparation of P-SbA was reported previously by Caletka and Konečný[12] and Jolivet and Lefebre[13]. The water content of the air-dried P-SbA varied between 24 and 30% (w/w), depending on the humidity of the air.

Determination of the ion-exchange capacity

The elution curve of the hydrogen ions liberated by 0.2 M ammonium nitrate solution is shown in Fig. 1. The ion exchange proceeds rapidly at first, but the elution continues for a long period. Hydrogen ions were still being liberated even after passage of 30 fraction numbers (165 ml) of ammonium nitrate solution, and the capacity was calculated up to this point. The capacity was found to be 1.4 mequiv./g or 2.0 mequiv./ml.
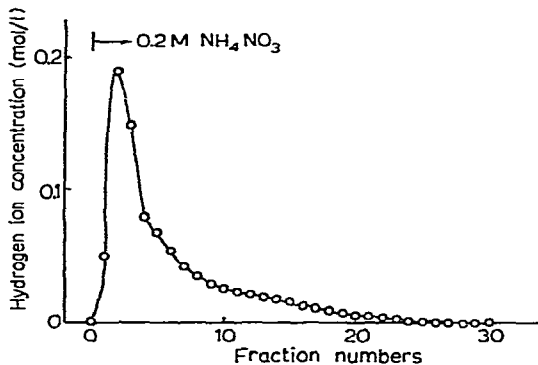

Fig. 1. Elution curve of hydrogen ions on P-SbA with 0.2 M ammonium nitrate solution.

Distribution coefficients

The values of K_d and the separation factor, $\alpha(A/B) = K_{dA}/K_{dB}$, where A and B are alkali metals, are summarized in Table I, values on other ion exchangers being included for the comparison.

The selectivity for alkali metals on P-SbA decreases in the order Cs > Rb > K > Na > Li, as shown with sulphonate-type organic resins. The separation factors for the Rb–K and Cs–Rb pairs on P-SbA are more favourable than those obtained on Amberlite IR-120. Smit et al.[6] reported separation factors of $\alpha(Cs/Rb) = 1.2$ and $\alpha(Rb/K) = 1.1$ from the equilibrium determinations of K_d for individual alkali metals on Dowex 50 in ammonium nitrate solution.

TABLE 1

K_d VALUES FOR ALKALI METALS ON VARIOUS ION-EXCHANGERS

Ion exchanger	Solution	Parameter*	Li	Na	K	Rb	Cs
P-SbA	0.05 M NH$_4$NO$_3$	K_d	15.6	18.0	32.0	74.8	270
		α		1.2	1.8	2.3	3.7
Amberlite IR-120	0.2 M HNO$_3$	K_d	19.5	30.0	64	88.5	100
		α		1.5	2.1	1.3	1.2
Dowex 50W-X8 (NH$_4$)**	0.1 M NH$_4$NO$_3$	K_d	—	0.95	1.33	1.42	1.69
		α			1.5	1.1	1.2
Ammonium molybdophosphate**	0.1 M NH$_4$NO$_3$	K_d	—	—	5.0	193	5443
		α				39	28
Zirconium phosphate	0.1 M HNO$_3$	K_d	15.0	41	140	390	910
		α		2.7	3.4	2.8	2.3

* α = separation factor for neighbouring ions.
** Data from ref. 6.

Log–log plots of K_d versus [NH$_4^+$] are shown in Fig. 2. The slope of dlog K_d/dlog[NH$_4$] was about −1 for all alkali metals, as expected for "ideal" 1:1 ion-exchange reactions.

Separation of alkali metals on the column of P-SbA

Higher separation factors for the Rb–Cs pair were obtained on the various inorganic ion exchangers, e.g., zirconium phosphate[14–16], zirconium tungstate[7,17] and heteropoly acid salts[6,18,19], and good separations have been reported for trace
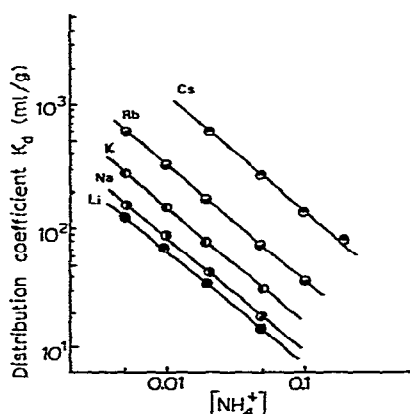

Fig. 2. Distribution coefficients for alkali metals on P-SbA at different concentrations of ammonium ions.

amounts on these ion exchangers. However, they have a slow ion–exchange rate so that effective separations cannot be achieved without overlap of the elution bands for micro- and macro-amounts of alkali metals[20–22]. Good separations of the Rb–Cs pair were achieved only by using a heated column thermostated with a water jacket at 50–80°. Extremely high separation factors for K–Rb and Cs–Rb on heteropoly acid salts have been reported, e.g., ammonium and thallium 12-molybdophosphate gave α(Cs/Rb) values of 26 and 33, respectively. Column beds of these heteropoly acid salts up to a few millimeters in depth may be available for the analytical separation of trace amounts of radioactive elements, but deeper beds of these materials do not allow practical flow-rates. Improved separations of macro-amounts were effected by using a column consisting of a physical mixture of heteropoly acid salts with asbestos fibre or filter-paper pulp.

On elution through a column of P-SbA, a satisfactory separation of Li–K–Rb–Cs was achieved with 0.1 M ammonium nitrate solution in the usual manner (Fig. 3). The individual elution curves for the alkali metals resemble the symmetrical bell-shaped peaks of the normal Gaussian function without tailing effects, whereas elution peaks with a sharp front and a tailing rear are often observed on inorganic ion exchangers which show isotherms of the Langmuir type[23,24]. Elution curves of the latter type are caused by the main portion of the solute band being eluted more rapidly than the leading front edge due to a limited number of sites available for adsorption as a function of concentration of the solute[24].
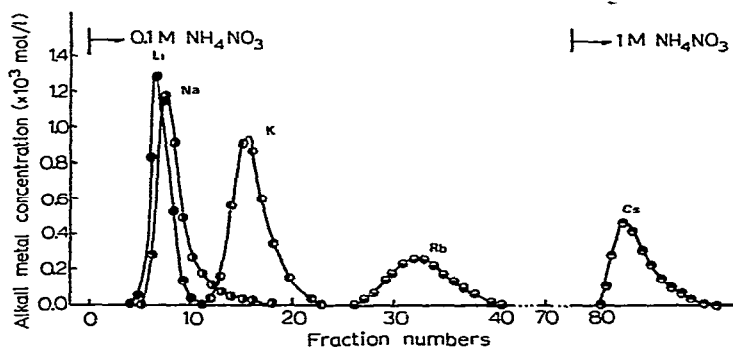

Fig. 3. Elution of alkali metal ions on P-SbA with 0.1 and 1 M ammonium nitrate solutions. Flow-rate, 0.3 ml/min; 1 fraction = 5.5 ml; alkali metals, 0.02 mmole each.

The symmetrical bell-shaped elution curves observed on P-SbA may be the result of the presence of a linear isotherm under the conditions used. On elution with 0.1 M ammonium nitrate solution, lithium, potassium and rubidium were eluted separately, while caesium was not eluted with up to 70 fraction numbers and then was eluted with 1 M ammonium nitrate solution (Fig. 3). Less effective separations were achieved with the Li–Na pair on the column used, as expected from the individual K_d values, even if more dilute ammonium nitrate solution was used as the eluent. When the eluent concentration was decreased to 0.05 M, potassium ions were separated from sodium ions, while rubidium ions were not eluted with up to 50 fraction numbers (Fig. 4). A satisfactory separation of rubidium from caesium was achieved with a
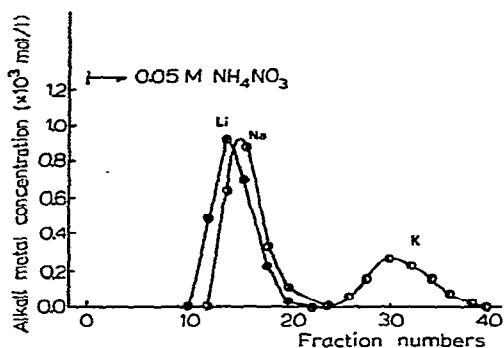
Fig. 4. Elution of Li, Na and K on P-SbA with 0.05 M ammonium nitrate solution. Flow-rate, 0.3 ml/min; 1 fraction = 5.5 ml; alkali metals, 0.02 mmole each.
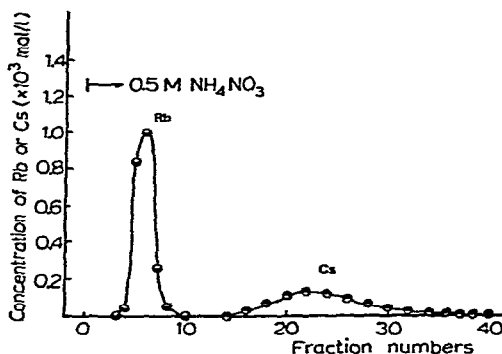
Fig. 5. Separation of Rb and Cs on P-SbA with 0.5 M ammonium nitrate solution. Flow-rate, 0.3 ml/min; 1 fraction = 5.5 ml; alkali metals, 0.02 mmole each.

sharp elution band by using 0.5 M ammonium nitrate solution as the eluent. The quantitative separations were performed with a 97% recovery of pure potassium from lithium and sodium, and with a 99% recovery of pure rubidium and caesium from the other alkali metals.

The P-SbA cation exchanger has good regeneration properties, and can therefore be used repeatedly under the usual column operation conditions.

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