

Synthetic Inorganic Ion-exchange Materials. XXXI. Ion-exchange Behavior of Tervalent Metals and Rare Earth Elements on Crystalline Antimonic(V) Acid Cation Exchanger

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The increasing order of ion-exchange selectivity for trivalent metal ions: $\text{Al}^{3+} \ll \text{Ga}^{3+} \leq \text{Yb}^{3+} < \text{Fe}^{3+} < \text{La}^{3+} < \text{In}^{3+}$, was established in 1 mol dm⁻³ nitric acid solution on a crystalline antimonic(V) acid (C-SbA) cation exchanger. Strong correlation was found between the selectivity and the effective ionic radii of these ions. Large separation factors for neighboring ions were obtained, as compared with the commercial ion exchange resin. An effective separation of aluminium(III)-iron(III) ion pairs and a group separation of gadolinium(III) and ytterbium(III) ions from lanthanum(III) ion were performed by using a relatively small C-SbA column (4 cm × 0.4 cm i.d.).

Various antimonic(V) acids behave as cation exchangers and can be prepared in three different species: crystalline, amorphous, and glassy.¹⁾ Among these antimonic(V) acids, crystalline antimonic(V) acid (C-SbA), $\text{Sb}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$, has received much attention during the last two decades, owing to its high selectivity for certain elements.²⁾ The C-SbA exhibits the increasing order of selectivity in microquantities: $\text{Li}^+ < \text{K}^+ < \text{Cs}^+ < \text{Rb}^+ < \text{Na}^+$ for alkali metals,³⁾ $\text{Mg}^{2+} < \text{Ba}^{2+} < \text{Ca}^{2+} < \text{Sr}^{2+}$ for alkaline earth metals,⁴⁾ and $\text{Ni}^{2+} < \text{Mn}^{2+} < \text{Zn}^{2+} < \text{Co}^{2+} < \text{Cu}^{2+} < \text{Cd}^{2+}$ for bivalent transition metals^{5,6)} in nitric acid media. Effective separations can be achieved for alkali metals,^{3,4,7)} the pairs of Mg^{2+} – Ba^{2+} , Ba^{2+} – Sr^{2+} , Cs^+ – Sr^{2+} ,⁸⁾ and Cd^{2+} –(Zn^{2+} , Cu^{2+}).^{5,6)} Adsorption reactions for all these ions obey the reversible ion-exchange reactions.^{9–11)}

Slightly different selectivity was observed on polyantimonic(V) acid (PAA)¹²⁾ and hydrated antimony pentoxide (HAP)¹³⁾: $\text{Rb}^+ < \text{Cs}^+ < \text{Na}^+$,¹²⁾ $\text{Cs}^+ < \text{Rb}^+ < \text{NH}_4^+ < \text{K}^+ < \text{Na}^+$,¹⁴⁾ and $\text{Ra}^{2+} < \text{Ba}^{2+} < \text{Ca}^{2+} < \text{Sr}^{2+}$.¹²⁾

No systematic study has been carried out for the selectivity of trivalent metals, including rare earth metals, on C-SbA.

On the other hand, the ion-exchange separations of rare earth metal ions are very difficult in nitric acid media, because of the extreme closeness of the chemical properties of individual rare earth elements. Chromatographic separations of rare earth elements on cation exchange resins have been reported by use of complexing agents, such as citrate, lactate, edta and α -hydroxyisobutyrate.¹⁵⁾ In recent years, radioactivation analysis is the only method which allows the determination of each individual rare earth element in high purity metals or rock samples. Even here, more effective mutual separation of rare earth elements may be needed, as well as better separation from the matrix.^{16–20)}

An improved selectivity for trivalent metal ions has been found on synthetic inorganic ion exchangers such as titanium arsenate,²¹⁾ zirconium tungstate,²²⁾ tin(IV) arsenate,²³⁾ and titanium tungstate.²⁴⁾

This paper describes the ion-exchange selectivity for micro-amounts of some trivalent metal ions and rare

earth metal ions on C-SbA cation exchanger in nitric acid media, and some applications to the chromatographic separation.

Experimental

Chemicals. Antimony pentachloride supplied by Yotsuhata Chemical Co., Ltd., was employed without further purification. Other chemicals (Wako Pure Chemical Industries, Ltd.) were of purity over 99.5%. The water used was prepared by distilling water and then passing it through a mixed bed of anion and cation exchange resins. The water showed a conductivity lower than 3×10^{-5} S cm⁻¹.

Sample Solutions and Determinations. Stock solutions containing 0.1 M (1 M = 1 mol dm⁻³) metal ion in 0.1 M nitric acid solution were prepared by dissolving weighed amounts of each metal, aluminium, indium, and lanthanum, and iron(III) nitrate nonahydrate and ytterbium(III) oxide in moderately concentrated nitric acid solution in order to prevent any hydrolysis with warming. The concentration of iron(III) ion was determined gravimetrically as iron(III) oxide.

For the measurement of equilibrated distribution coefficients of gadolinium(III), indium(III), lanthanum(III), and ytterbium(III) ions, aliquots of supernatant solutions were taken into polyethylene capsules and activated together with their standard metal ion solution in known amounts with the TRIGA II reactor at Musashi Institute of Technology (thermal flux, 4×10^{11} n cm⁻² s⁻¹; fast flux, 6.5×10^{10} n cm⁻² s⁻¹). The irradiating time was selected by reference to the thermal cross section and the resonance integral of each nuclide.²⁵⁾ After a cooling time appropriate for each radionuclide, the γ -spectra of the indicator nuclides were analysed with the "GAMA" system using Ge(Li) detector connected to 4096 channel analyser.²⁶⁾ The indicator nuclide and γ -energy used for determination were as follows: ⁷²Ga, 833 keV; ^{116m}In, 1508 keV; ¹⁴⁰La, 1595 keV; ¹⁷⁵Yb, 396 keV. Good linearity was obtained for the calibration curve of each metal ion.

The determination of iron(III) or aluminium(III) ions in microamounts was carried out by a Varian-Techtron 1100 atomic absorption spectrometer. For atomization of aluminium, a Varian-Techtron carbon rod atomizer equipped with an automatic sample dispenser was employed.

The emf titration method was employed for the determination of hydrogen ions in sample solution by using 0.1 mol dm⁻³ sodium hydroxide solution.

Preparation of C-SbA as an Ion Exchanger. The procedure was described in an earlier paper.¹⁾

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Distribution Coefficients (K_d). C-SbA (0.250 g) was immersed in 25.0 cm³ of a solution containing metal ion of 1×10^{-4} M in a nitric acid solution adjusted to a desired concentration with intermittent shaking at $(30 \pm 0.1)^\circ\text{C}$. The K_d values were determined by the following equation:

$$K_d = \frac{\text{Amount of metal ions in exchanger}}{\text{Amount of metal ions in solution}} \times \frac{\text{cm}^3 \text{ of solution}}{\text{g of exchanger}} \quad (\text{cm}^3/\text{g}).$$

The concentrations of the metal ions in solid and solution phases were deduced from the differences between the initial and the final concentrations in supernatant solution.

Column Operation. One μmol of gadolinium(III), lanthanum(III), and ytterbium(III) ions preactivated with reactor neutrons was loaded onto the C-SbA column of $4 \text{ cm} \times 0.4 \text{ cm}$ i.d. pretreated with 0.1 M nitric acid solution. Then, an appropriate eluant was passed through with a flow rate of $0.3 \text{ cm}^3/\text{min}$. The effluent was collected in test tubes by using a photosensitive drop count-type fraction collector (Ohtake Works, Ltd., Japan), followed by γ -counting with a Ge(Li) detector connected to a Northern 1705 1024 channel analyzer.

Thermal Analysis and X-Ray Study. These were carried out in the manner described previously.¹¹⁾

Results and Discussion

The results of the DTA, TGA, and X-ray studies of C-SbA in hydrogen form showed a good agreement with the earlier results.^{1,27)}

Ion-exchange Selectivity. The time dependence of adsorption for different metal ions showed that the equilibrium was attained within about 20 d for indium(III) and lanthanum(III) ions (Fig. 1). An extremely slow rate of adsorption for iron(III) ion was observed, about 100 d being required. The variety of time dependence from element to element may be considered to reflect the rigid structure of the C-SbA cation exchanger, as described earlier.⁹⁾

The plot of $\log K_d$ vs. $\log [\text{HNO}_3]$ showed a linear relationship with a slope of -3 , indicating an "ideal" 3:1 ion-exchange reaction (Fig. 2).

The observed K_d values (logarithmic scale) in 1 M nitric acid solution were plotted against the atomic number (Fig. 3 top). The profile parallels the change in the effective ionic radii (EIR)²⁸⁾ (Fig. 3 bottom).

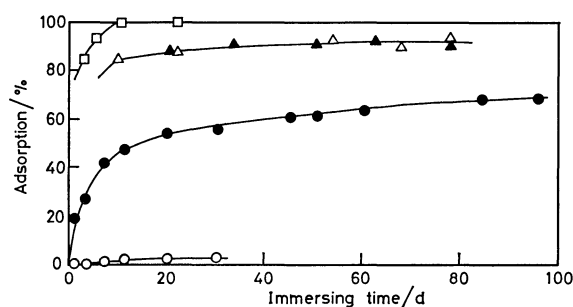


Fig. 1. Time dependence of adsorption of trivalent metal ions on C-SbA.

Ions and concentrations of HNO_3 ; \square : La (0.1 M), \triangle : La (1.0 M), \blacktriangle : In (1.0 M), \bullet : Fe (1.0 M); \circ : Fe (4.0 M).

The maximum K_d value was found for ions having about 1 \AA of the EIR. Such correlation has been also observed for alkali, alkaline earth, and bivalent transition metal ions, e.g., Na^+ (1.02 \AA), Ca^{2+} (1.00 \AA), Cd^{2+} (0.95 \AA), and Hg^{2+} (1.02 \AA). The low K_d values were observed for metal ions having an EIR of about 0.7 \AA , e.g., Li^+ (0.74 \AA), Mg^{2+} (0.72 \AA), and Ni^{2+} (0.700 \AA).^{5,8-11,29,30)} Thus, the ion-exchange reactions are favorable for the ions possessing an EIR of about 1 \AA on the C-SbA, if there is a similar situation for the exchange reaction of trivalent metal ions

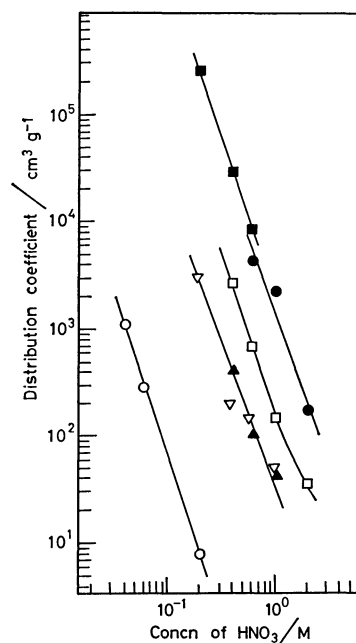


Fig. 2. Distribution coefficients of trivalent metal ions on C-SbA as a function of concentration of HNO_3 . Marks, \blacksquare : In, \bullet : La, \square : Fe, \blacktriangle : Yb, \circ : Al, \triangle : Ga.

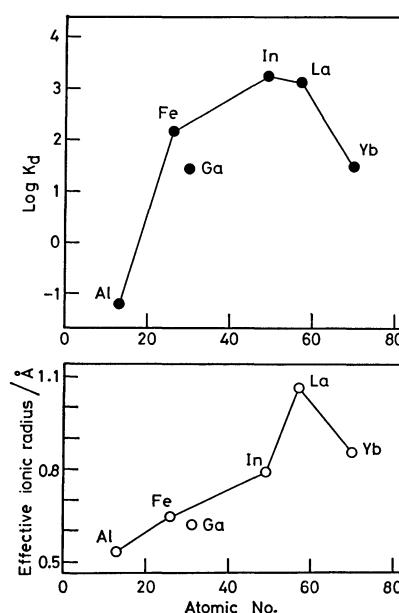
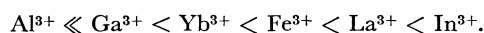


Fig. 3. Relations between changes in K_d values in 1 M HNO_3 and effective ionic radii with atomic number.

on the C-SbA.

In aqueous solution, the cations such as Ni^{2+} and Al^{3+} have an octahedral primary solvation shell.³¹⁾ If in the C-SbA the exchanging cations maintain a configuration similar to that in the aqueous solution, the electrostatic forces between ion-exchange sites and the hydrated cations may be less than in the case of partially hydrated or non hydrated cations. A thermodynamic treatment of the ion-exchange reactions reveals that the cations having the EIR of 1.0\AA , such as Na^+ and Cd^{2+} , are exchanged as less hydrated cations in the C-SbA with rigid structure than those in aqueous solution.^{9,29)} If the less hydrated cations are exchanged, the electrostatic force may be increased more than in the case in fully hydrated cations. When a large cation such as Cs^+ is exchanged in the C-SbA, the electrostatic force is less than small cations because of the low electron density for large cations.³⁰⁾ Therefore we conclude that the C-SbA has an ion-exchange site energetically preferable for the ions with an EIR of about 1\AA .

The C-SbA cation exchanger showed the following selectivity sequence for trivalent metal ions, in increasing order:



Larger separation factors, $\alpha(\text{A/B}) = K_d^{\text{A}}/K_d^{\text{B}}$, were observed on the C-SbA, as compared with those on strong acid-type cation exchange resin³²⁾ (Table 1). The selectivity order for trivalent metal ions on the HAP was found to be in the increasing order: $\text{Fe}^{3+} < \text{In}^{3+} < \text{Sc}^{3+} < \text{Yb}^{3+} < \text{Ce}^{3+} < \text{Eu}^{3+}$ in 1 M nitric acid solution.¹³⁾

Separation of Aluminium(III) and Iron(III) Ions.

The separation factor for the pair is very small on organic ion-exchange resin in nitric acid media,³²⁾ and it is difficult to separate them without use of a complexing agent such as ammonium tartrate and citrate. Vydra and Galba³³⁾ have achieved the separation of aluminium(III) from iron(III) ions on hydrous silica by using their hydrolytic products. It is evident from the study of the separation factor for this pair in nitric acid media that their effective separation will be much more favorable on the C-SbA.

When 110 cm^3 of 0.1 M nitric acid solution was used as an eluant, 66% of aluminium(III) ion loaded on the C-SbA was eluted, with a sharp peak followed by a long tail. This may be due to the very slow rate of ion-exchange. It is known that addition of

ammonium nitrate improves the elution characteristics for sodium ions.⁷⁾ A similar effect was observed for ions studied in the present work, except for iron(III) ion. Therefore a mixed solution of nitric acid and ammonium nitrate was employed for more rapid separation.

When a mixed solution of 0.1 M nitric acid and 0.05 M ammonium nitrate was used as an eluant, aluminium(III) ions were detected from the second fraction and eluted quantitatively with a elution volume of 65 cm^3 . More effective elution was achieved by the eluant of a mixed solution of 0.1 M nitric acid and 0.1 M ammonium nitrate: only about a half of the eluant volume was needed for the complete elution (Fig. 4).

Iron(III) ions were not eluted with 70 cm^3 of 0.5 M nitric acid solution. When 6 M nitric acid solution was injected, the iron(III) ions were eluted with a sharp front edge, followed by a strong tailing effect. A mixed solution of 6 M nitric acid and 2 M ammonium nitrate as an eluant showed a similar elution curve. This may be due to a slow rate of ion-exchange for iron(III), as expected from Fig. 1. Thus, 6 M hydrochloric acid was more effective (Fig. 4), owing to the negatively charged chloride complex of the iron(III) ion. Thus, an effective separation was achieved.

Elution Behavior of Gadolinium(III), Ytterbium(III), and Lanthanum(III) Ions. Since separation factors for

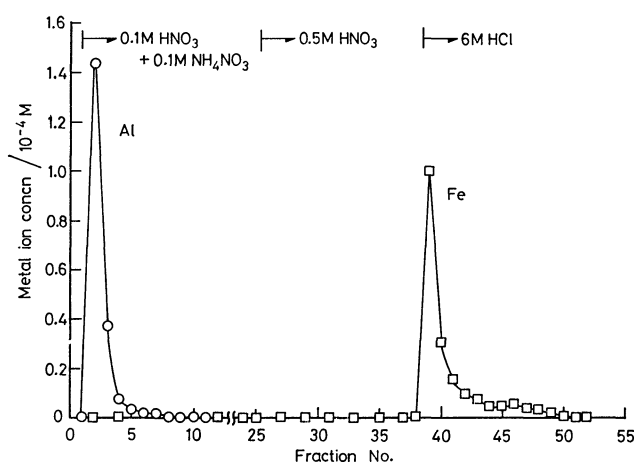


Fig. 4. Separation of Al^{3+} - Fe^{3+} with C-SbA column. One fraction = 5 cm^3 . Column size, $4 \times 0.4\text{ cm}$ i.d. Flow rate, $0.3\text{ cm}^3\text{ min}^{-1}$.

TABLE 1. K_d VALUES AND SEPARATION FACTORS (α)^{a)} OF TRIVALENT METAL IONS ON C-SbA IN 1 M HNO_3 SOLUTION

Ion exchanger	Ions	Al	Ga	Yb	Fe	La	In
C-SbA	$K_d/\text{cm}^3\text{ g}^{-1}$	6.39×10^{-2}	3.25×10	3.25×10	1.50×10^2	1.34×10^3	1.80×10^3
	α		509	1.00	4.62	8.93	1.34
Ion exchanger	Ions	Fe	Al	Ga	In	Yb	La
Bio-Rad ^{b)} AG50W-X8	$K_d/\text{cm}^3\text{ g}^{-1}$	74	79	94	118	193	267
	α		1.0 ₇	1.1 ₉	1.2 ₅	1.6 ₃	1.3 ₈

a) Separation factor for neighboring ions. b) Ref. 32.

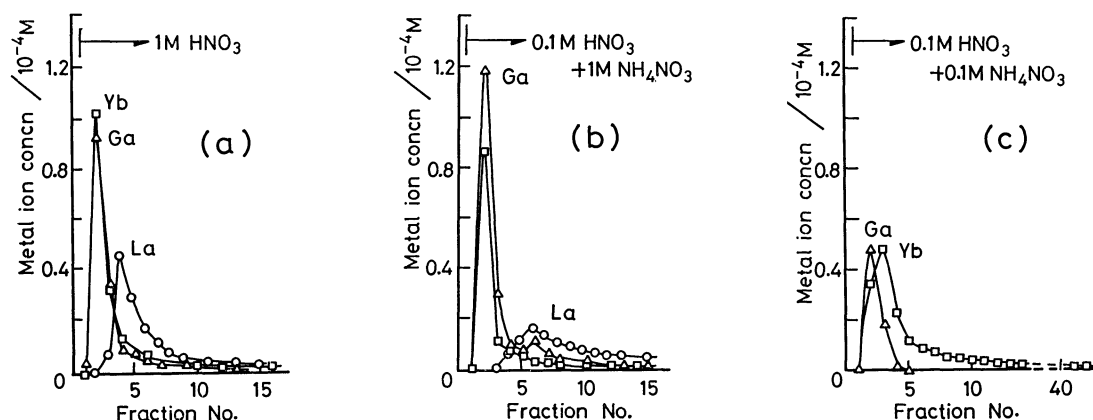


Fig. 5. Elution curves of Ga^{3+} , Yb^{3+} , and La^{3+} with C-SbA column. One fraction = 5 cm^3 . Column size, $4 \times 0.4 \text{ cm}$ i.d. Flow rate, $0.3 \text{ cm}^3 \text{ min}^{-1}$.

neighboring ions are very small on strong acid-type cation exchange resin in nitric acid media, mutual separations of these trivalent metal and rare earth metal ions can usually be achieved by using aqueous complexing agents or aqueous-organic solvent mixtures.³⁴⁾ However, even if such a technique is used, much eluant is required for these separations with a large column (e.g., 10 mm i.d. $\times 730 \text{ mm}$ h).¹⁸⁾

On the C-SbA, no ytterbium(III) ions were eluted, but gadolinium(III) ions were partly eluted with 95 cm^3 of a mixed solution of 0.1 M nitric acid and 0.05 M ammonium nitrate. A mixed solution of 0.2 M nitric acid and 0.05 M ammonium nitrate as an eluant showed a similar elution curve for gadolinium(III) ion. A more effective elution was observed for these cations by using a mixed solution containing ammonium nitrate at relatively high concentration (1 M), as in the case of aluminium(III) ions.

Lanthanum(III) ion was not eluted up to 40 cm^3 of 0.5 M nitric-acid solution, and incomplete elution was observed up to 200 cm^3 of the eluant, with a yield of 45%.

Elution peaks with tailings were observed for all elements when 1 M nitric acid (Fig. 5a) and a mixture of 0.1 M nitric acid and 1 M ammonium nitrate (Fig. 5b) were employed as the eluants. The elution order agreed with that of the batch equilibrium data.

The yields up to 16 fractions with 1 M nitric acid solution as an eluant were 95, 89, and 75% for ytterbium(III), gadolinium(III), and lanthanum(III) ions, respectively (Fig. 5a). When a mixed solution of 0.1 M nitric acid and 1 M ammonium nitrate was used as an eluant, these metal ions were eluted with the yields of 70, 65, and 44% for gadolinium(III), ytterbium(III), and lanthanum(III) ions, respectively, up to 13 fractions (Fig. 5b).

The effective group separation was achieved for gadolinium(III) and ytterbium(III) ions from lanthanum(III) ion by using a mixed solution of 0.1 M nitric acid and 0.1 M ammonium nitrate as an eluant (Fig. 5c), while the lanthanum(III) ions adsorbed were completely eluted with a 2 M nitric acid solution. Thus, the C-SbA column can be used repeatedly.

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