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Synthetic Inorganic Ion-Exchange Materials. LII. Ion-Exchange Selectivities of Crystalline Antimonic Acid for Tervalent Metal Ions

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The determination of selectivity coefficients for tervalent metal ions/hydrogen ions on cubic crystalline antimonic acid (C-SbA) was carried out for Ga^{3+}, Fe^{3+}, Ce^{3+}, Sm^{3+}, Y^{3+}, Sc^{3+}, and In^{3+} by batch equilibration at 30, 45, and 60 °C in nitric acid media. The selectivity in microamounts showed: $Al^{3+}<Tm^{3+}<Ga^{3+}<Yb^{3+}=Y^{3+}<Er^{3+}<Dy^{3+}<Fe^{3+}<Eu^{3+}<Sm^{3+}<Ce^{3+}<La^{3+}<Sc^{3+}=In^{3+}$. The ion-exchange isotherms of the systems of tervalent metal ions/hydrogen ions have also been studied on C-SbA. The selectivity coefficients in logarithm scale vs. equivalent fraction of metal ions in exchanger showed almost straight line, indicating monofunctional site with steric effect. In order to interpret the selectivity in microamounts of metal ions, hypothetical equilibrium constant was determined by extrapolating to zero loading of metal ions in C-SbA. From these values, the hypothetical thermodynamic data were calculated and evaluated.

During the last two decades much attention has been paid to the development of synthetic inorganic ion exchange materials with higher selectivities and resistance at high temperatures and in intense radiation fields than those of commercial ion-exchange resins.[1-6)]

Our works on the systematic studies on adsorption behavior of the hydroxides and hydrous oxides of multivalent metals indicated that "so-called" antimonic acid behaved as an excellent cation exchange material.[7,8)] Further studies showed that the antimonic acid can be classified into amorphous, glassy and crystalline materials by different preparative conditions, regardless of starting materials.[9)] Recently, monoclinic crystalline antimonic acid was synthesized by treating $LiSbO_3$ with 11 mol dm^{-3} HNO_3 and showed an extremely high selectivity for lithium ion.[10,11)] Among them, cubic crystalline antimonic acid (C-SbA) showed excellent ion-exchange properties and an unusual selectivity for various metal ions, compared to strong acid-type cation exchange resins.[13)]

The increasing order of selectivity in microamounts shows; $Li^+ \ll K^+ < Cs^+ < Rb^+ \ll Na^+$ for alkali metals,[12-14)] and $Mg^{2+}<Ba^{2+}<Ca^{2+}<Sr^{2+}$ for alkaline earth metals.[15,16)]

The similar unusual selectivity was observed for bivalent transition metals[17,18)] and tervalent metals.[19)] It has been known that the selectivity on inorganic ion exchangers strongly depends on the loading of metal ions in the exchangers. An ion-exchange study over various exchange composition may be needed for understanding of their selectivities. However, it is very difficult to study full range of the ion-exchange composition because of incomplete exchange for the limit of steric reason. Moreover, the overall thermodynamic data obtained are not so accurate for those systems, because of long extrapolation from experimental values.

The present paper has been concerned with the interpretation of the selectivity of M^{3+}/H^+ system for "zero loading" of metal ions in C-SbA. From the selectivity coefficient, the hypothetical thermodynamic data may be derived.

Theoretical

The ion exchange process may be represented by the following equation for tervalent metal cation/hydrogen ions system.

$$3\bar{H}^+ + M^{3+} \rightleftarrows \bar{M}^{3+} + 3H^+ \tag{1}$$

where the bar refers to solid phase, and M^{3+} and H^+ are tervalent metal and hydrogen ions.

The thermodynamic equilibrium constant, K, of the above reaction can be defined as

$$K = \frac{m_H^3 \bar{X}_M \, \gamma_H^3 \bar{f}_M}{m_M \bar{X}_H^3 \, \gamma_M \bar{f}_H^3} = K_H^M \frac{\bar{f}_M}{\bar{f}_H^3} \tag{2}$$

where K_H^M is defined as the corrected selectivity coefficient. The m_H and m_M are molalities of the cations in solution, γ_H and γ_M are the ionic activity coefficients of H^+ and M^{3+} in solution phase, $\bar{f}_H$ and $\bar{f}_M$ are those in solid phase, and $\bar{X}_H$ and $\bar{X}_M$ are equivalent fractions of H^+ and M^{3+} in the solid phase. The values of the ionic activity coefficient ratio (γ^3_H/γ_M) in solution can be calculated from the following equation.[20)]

$$\log(\gamma_H^3/\gamma_M) = 6\frac{S\, I^{1/2}}{1+A\, I^{1/2}} \tag{3}$$

where A and I are the distance of the nearest approach and the ionic strength, and

$$S = 1.8252 \times 10^6 (\rho/\varepsilon^3 T^3)^{1/2}$$

where ρ is the density of water, ε is the dielectric constant of water, and T is the absolute temperature of the system.

The thermodynamic equilibrium constant can be

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evaluated by using a simplified form of the Gaines-Thomas equation,[21] Eq. 4, assuming that the change of water activity in the C-SbA and in the solution is neglected.

$$\ln K = -(Z_M - Z_H) + \int_0^1 \ln K_H^M \, d\bar{X}_M \tag{4}$$

Sometimes, the graph of $\ln K_H^M$ against $\bar{X}_M$, which refers to the Kielland plot,[22] is linear with some inorganic ion exchangers, as follows;

$$\ln K_H^M = 4.606\, C\, \bar{X}_M + (\ln K_H^M)_{\bar{X}_M \to 0} \tag{5}$$

where the term C is called the Kielland coefficient and $4.606C$ is the slope of the line, and $(\ln K_H^M)_{\bar{X}_M \to 0}$ is the value $\ln K_H^M$ when $\bar{X}_M = 0$.

Some investigators have normalized uptakes with the maximum limit of exchange, $(\bar{X}_M)_{max}$, in the case where complete exchange is not obtained. However, this treatment does not allow a comparison between species which are exchanged to different extent.[16,23]

The normalization for C-SbA is based on the assumption that one SbOH group gives one hydrogen ion available for ion exchange. Thus, the theoretical capacity of 5.056 mequiv g^{-1} was used from the experimental formula of $Sb_2O_5 \cdot 4H_2O$.[16]

Experimental

Preparation of C-SbA. The C-SbA was prepared as described previously;[9] the precipitate obtained by hydrolysis of antimony pentachloride solution (1 : 1) was kept in the mother solution at 40 °C for over 20 d in order to enhance crystallization, and then washed with cold demineralized water until free from chloride ion with an aid of centrifuge (about 10000 rpm). After drying the product was ground and sieved (100—200 mesh size). The collected sample was rewashed with demineralized water in order to obtain clear supernatant solution in the following batch equilibrium experiments.

Distribution Coefficient (K_d). The K_d values were determined by equilibrating C-SbA in hydrogen ion form with a solution containing 1×10^{-4} M (1 M=1 mol dm^{-3}) metal ions and nitric acid at different concentrations. The ratio of volume of the solution to weight of C-SbA was kept in 100 ($cm^3 g^{-1}$). The K_d values of metal ions were calculated by using following expression;

$$K_d = \frac{\text{amount of metal ions in exchanger}}{\text{amount of metal ions in solution}} \times \frac{\text{cm}^3 \text{ of solution}}{\text{g of exchanger}} \tag{6}$$

Ion-Exchange Equilibria. In the forward reaction, the C-SbA in H^+ form was immersed in a mixed solution of varying ratio of the metal nitrate/nitric acid in a sealed glass tube with intermittent shaking at 30±0.1, 45±0.1, and 60±0.1 °C. The ratio of volume of mixed solution to weight of C-SbA was kept in 100 ($cm^3 g^{-1}$). The ionic strength in the equilibrium was adjusted to 0.2. The equilibrium concentrations in the solid phase and in aqueous phase were deduced from the change of M^{3+} and H^+ concentration relative to the initial concentration of the solution. The concentration of metal ions in the solutions was determined by spectrophotometric analysis.[24-26] Neutron activation analysis was employed for cross checking the analytical data for Sc, Sm, Eu, and Ce. The emf titration method was employed for determining the H^+ concentration with a standard sodium hydroxide solution.

Results and Discussion

Distribution Coefficient (K_d). Time dependence of adsorption for different metal ions showed that the equilibrium was attained within 20 d for Sc^{3+}, Tm^{3+}, and Eu^{3+}, and about 30 d for Y^{3+} (Fig. 1) The variety of the time dependence from element to element may be due to the rigid structure of C-SbA and rate of the exchange between hydrated water for the element and bulk water molecules in the aqueous solution.

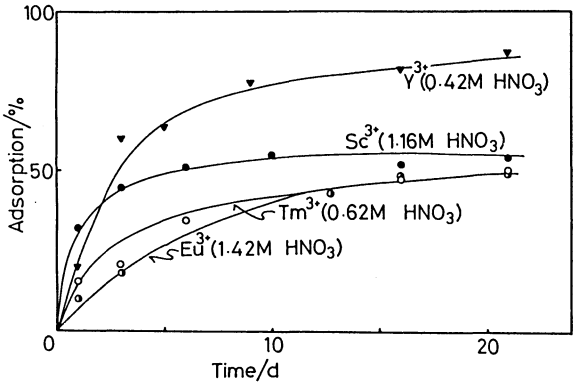

Fig. 1. Time dependence for the adsorption of rare earth ions on C-SbA. Initial concn of metal ions; 1.0×10^{-4} mol dm^{-3}. C-SbA; 0.50 g. Total vol.; 50.0 cm^3. Temp; 30 °C.

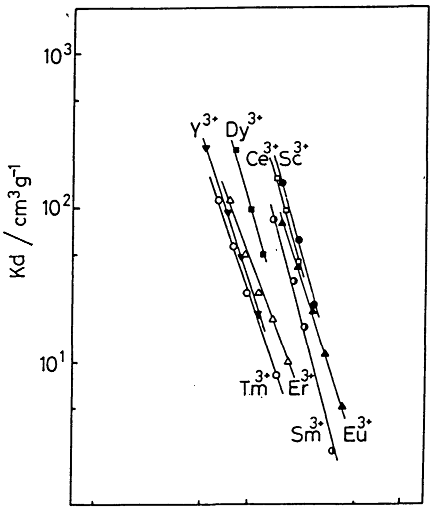

Fig. 2. Logarism K_d values of various metal ions vs. log[HNO_3] on C-SbA. Initial concn of metal ions; 1.0×10^{-4} mol dm^{-3}. C-SbA; 0.20 g. Total vol.; 20.0 cm^3. Temp; 30 °C.

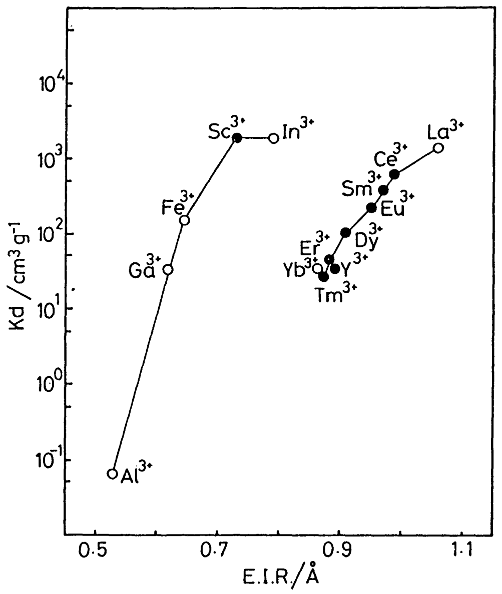

Fig. 3. The K_d of tervalent metal ions as a function of effective ionic radii of metal ions. ●: this work, ○: from Ref. 19.

The log-log plots of K_d vs. [HNO_3] showed that the slopes of dlog K_d/dlog[HNO_3] are about the same as the valency of metal ions studied, indicating the "ideal ion-exchange reaction" (Fig. 2). The equilibrium K_d values in logarithm scale of various tervalent metal ions on C-SbA were plotted against effective ionic radii (EIR)[27] of the metal ion in Fig. 3, after normalizing to a 1 M nitric acid solution. It was difficult to determine the K_d values experimentally higher than 10^3 for detection limit of the spectrophotometric analysis.

The following selectivity series were found for microamounts of tervalent metal ion on C-SbA in nitric acid solution;

$Al^{3+}<Tm^{3+}<Ga^{3+}=Yb^{3+}<Y^{3+}<Er^{3+}<Dy^{3+}<Fe^{3+}<Eu^{3+}$
$<Sm^{3+}<Ce^{3+}<La^{3+}<Sc^{3+}=In^{3+}$

Two different selectivity series were found for Al^{3+}, Ga^{3+}, Fe^{3+}, and In^{3+}, and from Tm^{3+} to La^{3+} on C-SbA. The difference in the electron configuration of the ion-exchange cations may be responsible for the results; the latter takes the $s^2p^6f^n$ configuration and the former takes a different configuration. The log K_d values on BIO-RAD AG 50W-X8 increase slightly with increasing EIR[27,28] of exchanging metal ions because of its elastic structure.

Kielland Plot. It has been known that the selectivity on inorganic ion exchangers is much dependent on the concentration of metal ions in the exchanger phase because of their rigid structure mentioned above. It is known that large steric effect may arise in a rigid exchanger which undergoes little swelling or shrinkage, if there is a large difference in the ionic crystal radii of the two exchanging cations.

Among the ion-exchange system of tervalent metal ions/hydrogen ions, Al^{3+}, Ga^{3+}, Fe^{3+}, Sc^{3+}, Y^{3+}, Sm^{3+}, and Ce^{3+}/H^+ were selected in order to interpret the selectivity of tervalent metal ions. The Kielland plot showed fairly good straight line for metal ions/H^+ systems studied (Figs. 4-1 to 4-3). The $\ln K_H^M$ values decreased gradually with increasing $\overline{X}_M$, indicating that the steric effect depends on a variety of the exchanging metal ion. The Kielland plots of different tervalent metal ions/H^+ system at 30 °C are summarized in Fig. 4-4. Moving the axis of abscissa from left to right upto $\overline{X}_M=0.1$ in Fig. 4-4, the different selectivity sequences can be found as a function of

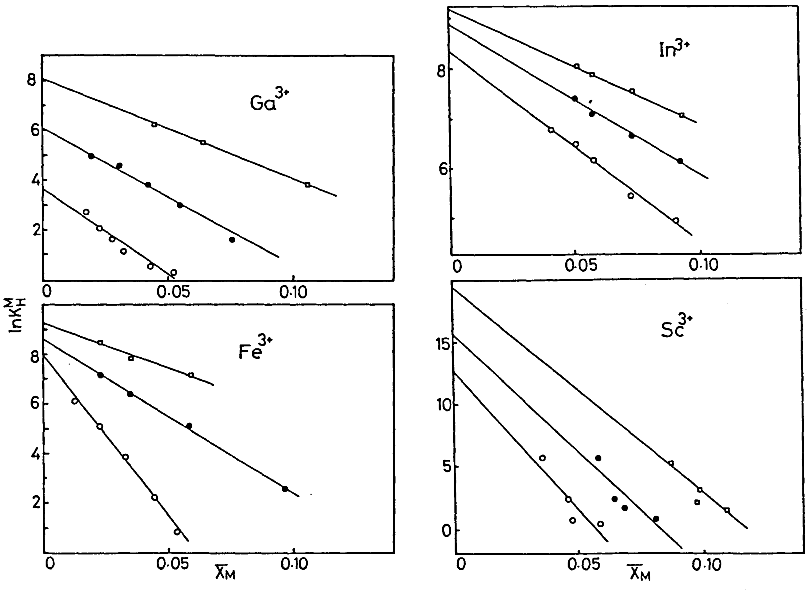

Fig. 4-1. The Kielland plots of Ga^{3+}, Fe^{3+}, In^{3+}, and Sc^{3+}/H^+ exchange systems on C-SbA. Ionic strength: 0.2. Temp, ○: 30, ●: 45, and □: 60 °C.

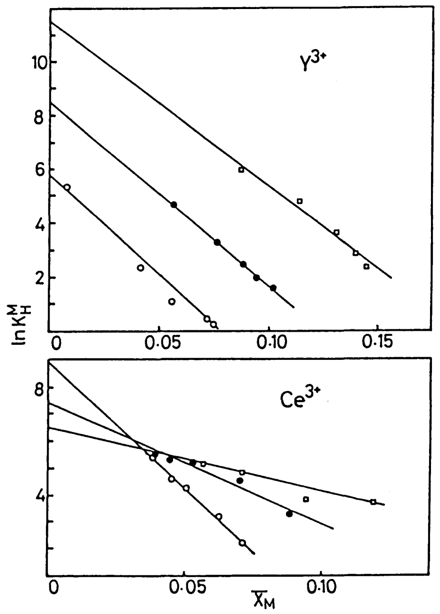

Fig. 4-2. The Kielland plots of Y^{3+} and Ce^{3+}/H^+ exchange systems on C-SbA. Ionic strength: 0.2. Temp, ○: 30, ●: 45, and □: 60 °C.

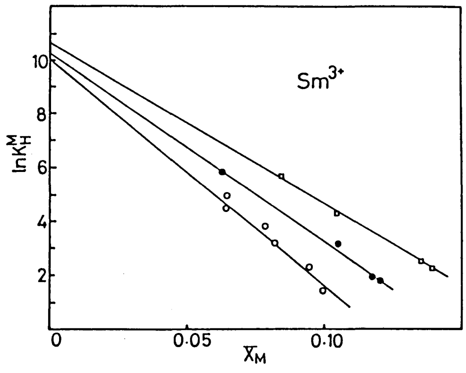

Fig. 4-3. The Kielland plots of Sm^{3+}/H^+ exchange systems on C-SbA. Ionic strength: 0.2. Temp, ○: 30, ●: 45, and □: 60 °C.

$\bar{X}_M$ to increase in the order $Al^{3+}<Ga^{3+}<Y^{3+}<Fe^{3+}<In^{3+}<Ce^{3+}<Sm^{3+}<Sc^{3+}$ for range of $\bar{X}_M=0$ to 0.008, and so on.

In general, when small cations in inorganic ion exchangers are exchanged with large cations in the solution, the ingoing ions are initially preferred and become progressively less preferred with increasing loading. This extent can be evaluated by the comparison of numerical values of Kielland coefficient, i.e., a large negative value of Kielland coefficient indicates a large steric effect.

The C/z, which is referred to equivalent Kielland coefficient,†† for different exchange systems are plotted as a function of EIR in Fig. 5, other published data[14,16,18] being included. This shows that cations

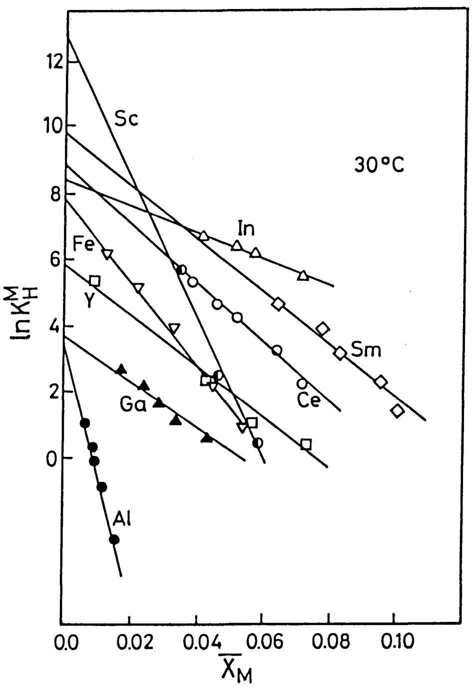

Fig. 4-4. The summarized Kielland plots of tervalent metal ions/H^+ exchange systems on C-SbA at 30 °C. Ionic strength: 0.2

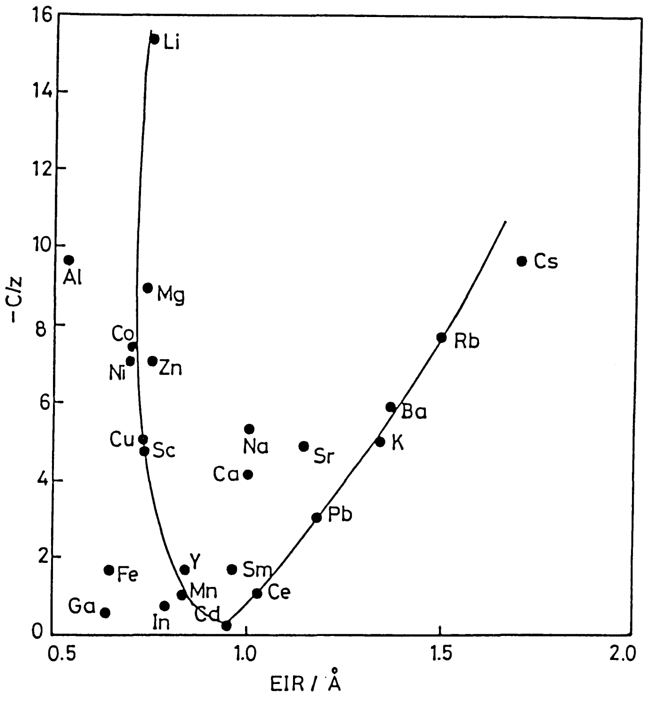

Fig. 5. The equivalent Kielland coefficients of tervalent metal ions/H^+ exchange systems on C-SbA vs. effective ionic radii (EIR) of the metal ions. EIR were taken from Table 1(a) of Shannon and Prewitt.[27]

with an effective ionic radius of about 1.0 Å enter the exchanger with minimum steric hindrance. The C-SbA has a rigid structure in which the change in the

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†† The Kielland coefficient for multivalent metal ions can be compared to those for alkali metal ions/H^+ system by this procedure.

lattice constant is less than 2% for the conversion from the hydrogen form to metal ion form.[14] The small cations, e.g., Li^+, Mg^{2+}, and Al^{3+}, are strongly hydrated in aqueous solution and may be exchanged with keeping their hydration shell. This brings large steric effect in the rigid structure of C-SbA.

The large cations, such as Ba^{2+}, Rb^+, and Cs^+, are less hydrated in the aqueous solution, and can be exchanged with a larger steric effect by increased crystal ionic radii of metal ions. Thus, the minimum steric effect may be interpreted in both contributions.

Hypothetical Thermodynamic Data. The thermodynamic equilibrium constant, K, can be evaluated from Eq. 2 or 4 by assuming that the linear relation between $\ln K_{\mathrm{H}}^{\mathrm{M}}$ vs. $\overline{X}_{\mathrm{M}}$ is valid over the entire range of $\overline{X}_{\mathrm{M}}$ from 0 to 1. However, high accuracy of these values is not obtained for long extrapolation of $\overline{X}_{\mathrm{M}}$ to 1.0. The hypothetical thermodynamic data in infinitesimal concentration were calculated for interpretation of the selectivity of metal ions in microamounts on C-SbA.

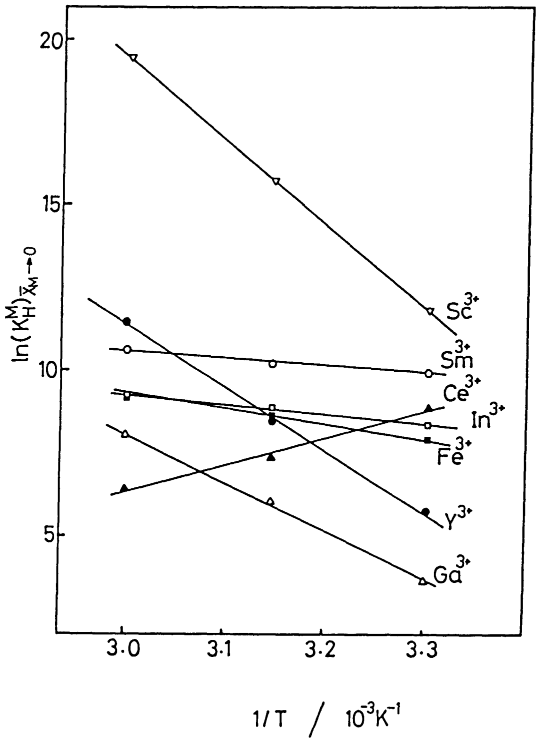

Fig. 6. Van't Hoff plots of $\ln(K_{\mathrm{H}}^{\mathrm{M}})_{\overline{X}_{\mathrm{M}}\to 0}$ on C-SbA.

The $(\Delta G^\circ)_{\overline{X}_{\mathrm{M}}\to 0}$ is defined as;

$$(\Delta G^\circ)_{\overline{X}_{\mathrm{M}}\to 0} = (-RT/z)\,(\ln K_{\mathrm{H}}^{\mathrm{M}})_{\overline{X}_{\mathrm{M}}\to 0} \tag{7}$$

The calculated $(\Delta S^\circ)_{\overline{X}_{\mathrm{M}}\to 0}$ and $(\Delta H^\circ)_{\overline{X}_{\mathrm{M}}\to 0}$ values can be regarded as a constant, because van't Hoff plots, $(\ln K_{\mathrm{H}}^{\mathrm{M}})_{\overline{X}_{\mathrm{M}}\to 0}$ vs. $1/T$, showed fairly good linearity over the entire range of temperature studied (Fig. 6). The $(\Delta G^\circ)_{\overline{X}_{\mathrm{M}}\to 0}$ values at 298 K were calculated by interpolating or extrapolating the determined $(\Delta G^\circ)_{\overline{X}_{\mathrm{M}}\to 0}$ values to 298 K. The calculated $(\Delta G^\circ)_{\overline{X}_{\mathrm{M}}\to 0}$ values at 298 K were plotted against EIR of the exchanging metal ions (Fig. 7). There appear two maxima which correspond to the selectivity series described above.

The ion-exchange reaction (1) can be separated into the hydration $(-\Delta Y_{\mathrm{hyd}})$ and ion-exchange processes (ΔY_{ex}) as follows;

$$1/3\ M^{3+}(aq) + H^+(gas) \rightleftarrows 1/3\ M^{3+}(gas) + H^+(aq) \qquad -Y_{\mathrm{hyd}}$$

$$1/3\ M^{3+}(gas) + \overline{H}^+ \rightleftarrows 1/3\ \overline{M}^{3+} + H^+(gas) \qquad \Delta Y_{\mathrm{ex}}$$

where the Y represents thermodynamic functions such as G, H, and S. The numerical values of ΔY° contribute to the difference between the thermodynamic function of the ion-exchange $(\Delta Y^\circ_{\mathrm{ex}})$ and that of hydration $(\Delta Y^\circ_{\mathrm{hyd}})$ of the cations on the basis of the $\Delta Y^\circ_{\mathrm{hyd}}=0$ of the reaction; $H^+(gas) \rightarrow H^+(aq)$. The value of $\Delta Y^\circ_{\mathrm{hyd}}$ can be calculated from Rosseinsky's table.[29]

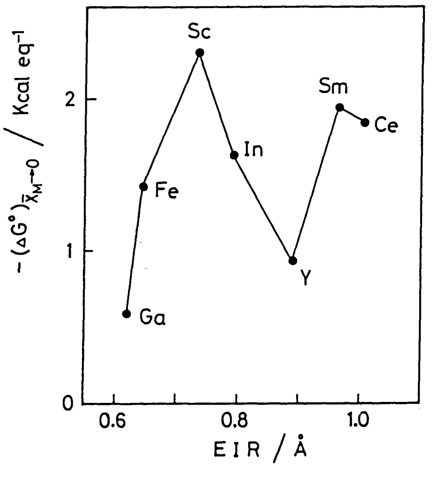

Fig. 7. $-(\Delta G^\circ)_{\overline{X}_{\mathrm{M}}\to 0}$ vs. EIR of metal ions.

Table 1. Hypothetical Thermodynamic Data for Zero Loading of Tervalent Metal Ions in C-SbA

Metal ions	EIR Å	$(\ln K_{\mathrm{H}}^{\mathrm{M}})_{\overline{X}_{\mathrm{M}}\to 0}$	C/z	$\Delta G^\circ_{\overline{X}_{\mathrm{M}}\to 0}$ kcal equiv^{-1}	$\Delta H^\circ_{\overline{X}_{\mathrm{M}}\to 0}$ kcal equiv^{-1}	$\Delta S^\circ_{\overline{X}_{\mathrm{M}}\to 0}$ cal deg.$^{-1}$ equiv^{-1}	$\Delta H^\circ_{\mathrm{hyd}}$ kcal equiv^{-1}	$\Delta S^\circ_{\mathrm{hyd}}$ cal deg.$^{-1}$ equiv^{-1}	$\Delta H^\circ_{\mathrm{ex}}$ kcal equiv^{-1}	$\Delta S^\circ_{\mathrm{ex}}$ cal deg.$^{-1}$ equiv^{-1}
Al^{3+}	0.53	3.5	−28.9							
Ga^{3+}	0.62	3.00	−4.94	−0.592	9.59	34.1	$-112._5$	−14.7	$-102._9$	19.4
Fe^{3+}	0.645	7.12	−9.39	−1.41	4.02	18.2	−88.0	−11.2	-83.9_8	7.0
Sc^{3+}	0.73	11.6_5	−16.4	−2.30	15.0_4	58.2	−51.1	−6.2	−36.1	52.0
In^{3+}	0.79	8.22	−2.81	−1.62	1.80	11.5	−66.6	−8.0	−64.8	3.5
Y^{3+}	0.89	4.8	−5.5	−0.947	12.5_6	45.2_9	−27.4	−4.6	-14.8_4	40.7
Sm^{3+}	0.964	9.82	−6.0	−1.94	1.52	11.6	-14.7_8	−5.07	-13.2_6	6.5
Ce^{3+}	1.034	9.30	−6.72	−1.84	−0.57	4.23	−4.64	−4.59	−5.2	−0.36

The calculated values of ΔY°, $\Delta Y^\circ_{\mathrm{hyd}}$, and $\Delta Y^\circ_{\mathrm{ex}}$ were summarized on Table 1.

Large numerical values of $(\Delta H^\circ)_{\bar{X}_M\to0}$ and $(\Delta S^\circ)_{\bar{X}_M\to0}$ were found on the systems of Sc^{3+} and Y^{3+}/H^+, as compared with those of other systems studied. The $\Delta S^\circ_{\mathrm{ex}}$ showed all positive value, except Ce^{3+}/H^+ system. An extremely high value was observed on the systems of Sc^{3+} and Y^{3+}/H^+.

If the ΔS° is zero, where the value of $\Delta S^\circ_{\mathrm{ex}}$ is equal to that of $\Delta S^\circ_{\mathrm{hyd}}$, this suggests that the exchanging cation in exchanger has the same hydration structure as that in aqueous solution. The positive value of $\Delta S^\circ_{\mathrm{ex}}$ may indicate that degree of freedom of metal ion increases in the cavity of C-SbA. Such an increase of $\Delta S^\circ_{\mathrm{ex}}$ may occur from dehydration of metal ions or net transfer of water molecules from solid phase to aqueous phase. When the less hydrated cations such as Rb^+ and Cs^+ are the ingoing cations, the degree of freedom may increase by the transfer of some water molecules from a C-SbA cage to the aqueous phase.

In order to understand the unusual selectivities on C-SbA, the values of $\Delta S^\circ_{\mathrm{ex}}$ were plotted against ionic hydration numbers,[30] h_i^∞ being taken from $\Delta S^\circ_{\mathrm{hyd}}$ (Fig. 8).

The h_i^∞ calculated from data of hydration entropy contains the primary and secondary hydration shells. The entropy of the hydration of an ion may be written as in Eq. 8.[31]

$$\Delta S^\circ_{\mathrm{hyd}} = R\ \ln(V_f/V_g) + S_A + S_B + S_C \tag{8}$$

where the $R\ \ln(V_f/V_g)$ term allows for the fact that the free volume (V_f) accessible to the aqueous solution is not the same as that in the gaseous phase (V_g). The term S_A is a contribution for water molecules forming the primary hydration shell, and the term S_C is the Born-model contribution for water outside the primary hydration shell. The term S_B is the contribution from water in the secondary shell. The values of S_B are probably positive (structure breaking effect) for all alkali and alkaline earth metal ions, except Li^+ and Mg^{2+}. Thus the results bring to form the Frank-Wen three zone model.[32] In zone A, water molecules in primary hydration shell are tightly bonded by the strong coulombic field of the ion. Zone B, interposing between zone A and C, is a structure breaking region.

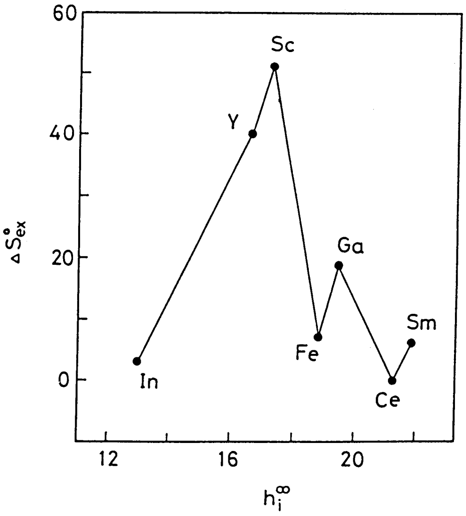

Fig. 8. The correlation between $\Delta S^\circ_{\mathrm{ex}}$ and hydration number (h_i^∞) for metal ions.

The zone B is less electrostrictive structure than zone A, and is less tetrahedrally coordinated than bulk water in zone C. If there is a contribution of coulombic force to the ion on exchange site enough to break the water structure of the hydration shell, the less hydrated ion can enter the narrow cavity in the exchanger. This may bring an increase in the $\Delta S^\circ_{\mathrm{ex}}$. The water molecules of metal ion having small EIR may be tightly bound by the strong coulombic field of the metal ions, such as Mg^{2+}, first-row bivalent transition metal ions and Al^{3+}. It is very interesting in the fact that the electron configuration of Sc^{3+} is essentially the same as that of Y^{3+} and similar numerical value of h_i^∞ is given for Sc^{3+} and Y^{3+} in aqueous solution.

When the coulombic force between the ion and the site is not strong enough to break water structure of the primary hydration shell, the small contribution of the $\Delta S^\circ_{\mathrm{ex}}$ may arise. The large contribution of the $\Delta S^\circ_{\mathrm{ex}}$ in the Sc^{3+} and Y^{3+}/H^+ systems may be due to both contributions of the net transfer of water molecules from solid phase to the aqueous solution and structure breaking of the water in exchanger.

The larger contribution of $\Delta S^\circ_{\mathrm{ex}}$ for Sc^{3+}/H^+ system than that of $(\Delta H^\circ)_{\bar{X}_{Sc}\to0}$ brings a large numerical value of $(\ln K_H^{Sc})_{\bar{X}_{Sc}\to0}$, as compared with the system for Y^{3+}/H^+.

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