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Mitsuo Abe[a]
[a] DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE TOKYO INSTITUTE OF TECHNOLOGY OOKAYAMA, TOKYO, JAPAN

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Synthetic Inorganic Ion-Exchange Materials. XXVII. A Study on Ion-Exchange Selectivity in Crystalline Antimonic(V) Acid and Hydrated Antimony Pentoxide for Various Metal Ions in Nitric Acid Media

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MITSUO ABE

DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
TOKYO INSTITUTE OF TECHNOLOGY
OOKAYAMA, MEGURO-KU, TOKYO 152, JAPAN

Abstract

A comparative study of ion-exchange selectivity was carried out between crystalline antimonic(V) acid (C-SbA) and hydrated antimony pentoxide (HAP). The extended plate theory was applied for evaluating the values of distribution coefficients of various metal ions on HAP from the retention results reported by Girardi et al. The results indicate that the ion-exchange selectivity of C-SbA is essentially compatible with that in HAP for 17 of 20 metal ions.

INTRODUCTION

During the last 20 years much attention has been paid to the development of synthetic inorganic ion-exchange materials for outstanding resistance to chemicals, high temperature conditions, and radiation dose, and for higher selectivities to certain elements than those in the commercial ion-exchange resins and natural inorganic ion-exchangers (*1–5*).

The "so-called" antimonic(V) acid behaves as an excellent cation-exchanger with high capacity and reasonable rates of adsorption and desorption based on our systematic studies of various hydrous oxides of polyvalent metals (*6–8*).

Three different types of antimonic(V) acids, amorphous, glassy, and crystalline, have been found by different preparations from the same starting substances (*9*). Among them, crystalline antimonic(V) acid (C–SbA) shows excellent selectivities for certain elements, which is much different from those on organic ion-exchange resins. Some effective separations were achieved with relatively small columns (1.0 to 6.0 cm in length) of C-SbA (*11*, *12*).

Girardi et al. (*13*) have reported that the retention properties of different radio-ions on columns of 11 ionic precipitates from different acid media were studied in about 2000 adsorption experiments. They found excellent retention properties of sodium ion even in nitric acid solution at high concentrations on hydrated antimony pentoxide (HAP) from the results of experiments for 34 metal ions.

We have determined the equilibrated distribution coefficients on C-SbA for various metal ions such as alkali metals, alkaline earth metals, transition metals, and noble metals (*11*, *14–16*).

The empirical formula can be represented by $Sb_2O_5 \cdot 4H_2O$ for C-SbA and $Sb_2O_5 \cdot 0.3H_2O$ for HAP, and X-ray diffraction pattern shows a cubic structure with $a = 10.38_4$ Å (C-SbA) and 10.32_6 Å (HAP), respectively. This paper describes similarities and differences in the selectivities for C-SbA and HAP.

EXPERIMENTAL

Preparation of C-SbA

The C-SbA was prepared as previously described (*9*).

Distribution Coefficients (K_d)

The equilibrated distribution coefficients of lead and iron(III) were determined by shaking 0.250 g of the C-SbA with 25.0 mL of a solution containing 1×10^{-4} M metal nitrate solution in a nitric acid solution at different concentrations. The amounts of metal ions adsorbed were determined from the difference between the initial and final concentration of the metal ions in the clear supernatant solution by using a Varian-Techtron 1100 atomic absorption spectrometer. The K_d values of other metal ions were taken from our results earlier (*11*, *14–16*).

Column Experiments

The ion-exchange columns used were 6.0 × 0.8 cm i.d., and column experiments were carried out at a flow rate of 0.6 mL/min for both C-SbA and Amberlite IR 120.

RESULTS AND DISCUSSION

Estimation of K_d Values from Retention Data for Various Metal Ions on Girardi's HAP Column

In order to compare the selectivities of C-SbA and HAP, the K_d values on the HAP column were evaluated from retention data reported by Girardi et al. (*13*). The HAP column is prepared with a 3-cm height and 0.7 cm internal diameter. The retention data are obtained by the following standardized method: A preliminary wash with 5 mL of the eluting solution was added before the sorption step and two succesive 15 mL fractions were passed through after the sorption step (5 mL) (*13*). These data are represented by the symbols ○ [completely eluted (over 97 %)], ◑ [partially retained (the black area is proportional to the amount retained)], and ● [completely retained (over 99 %) in the periodic table].

If half retention is performed for certain element, the following correlation from the plate theory may be obtained between the K_d value and the peak elution volume ($V_{\max}$):

$$V_{\max} = I + MK_d \tag{1}$$

where I and M are interstitial volume and the weight of exchanger in the column, respectively. The values of I (= 1.2 mL) and M (= 1.0 g) can be estimated from the results based on a value of the closest packing and density (0.87 g/mL) of HAP in the column reported by Girardi et al. (*13*).

The K_d value for the half retained was found to be 28.8 by assuming that $V_{\max}$ was 30.0 mL. The K_d values for 99 % retained and 97 % eluted can be estimated from application of the plate theory. In an extension of the plate theory of Martin and Synge (*17*) and Beukenkamp et al. (*18*), the $V_{\max}$ in Eq. (1) is also represented in terms of the distribution ratio (C) in a solution:

$$V_{\max} = I(1 + C) \tag{2}$$

If the elution curves show Gaussian distribution, the total number of theoretical plates in the column, p, was evaluated by

$$p = \left(\frac{2C}{1 + C}\right)\left(\frac{V_{\max}}{V_a - V_{\max}}\right) \tag{3}$$

where V_a is the volume eluted when the concentration of the elements in the eluate is equal to the value of (the maximum concentration of the elements/base of the natural system of logarithms). Unfortunately, the values of p cannot be evaluated directly because of lack of an elution graph for the HAP column.

As a first approximation, it is assumed that the elution curves obtained on the C-SbA column are quite similar to those obtained on the HAP column. Thus Eq. (3) can be used to evaluate p from the experimentally determined elution graph on C-SbA. It is known that the shape of elution curves depends on the chemical species, the concentration of the solute in the column, and the rates of adsorption and desorption. As a second approximation, the elution curves show Gaussian distribution because of tracer or microquantities of the elements in the eluate. The typical elution curves obtained for lithium ions on the C-SbA column are illustrated in Fig. 1. The calculated values for p were found to be 35.2 and 39.8 for the elution curves with 0.005 and 0.003 M nitric acid solution as the eluants, respectively. The values of p and the width (W_1/e) of the elution curves also depend on the retention volume. The theoretical plates per centimeter, P, were plotted against the standardized maximum elution volume (R) which is $V_{\max}$ per cross section of the column and per centimeter of the length (Fig. 2). A smaller value of P was observed on the C-SbA column than on the Amberlite IR 120 column at the same value of R. For elution of Amberlite IR 120 by a nitric acid solution at different concentrations, the relationship between P and R showed a straight line independent of the ionic species of the alkali metals. For the elution on the C-SbA, the relationship showed a straight line for individual ionic species with different slopes for the elution of alkali metals. The average value was taken to estimate P in the HAP column from the value of R. Thus the value was evaluated to be 40 for p in the HAP column of 3.0 cm length. The elution

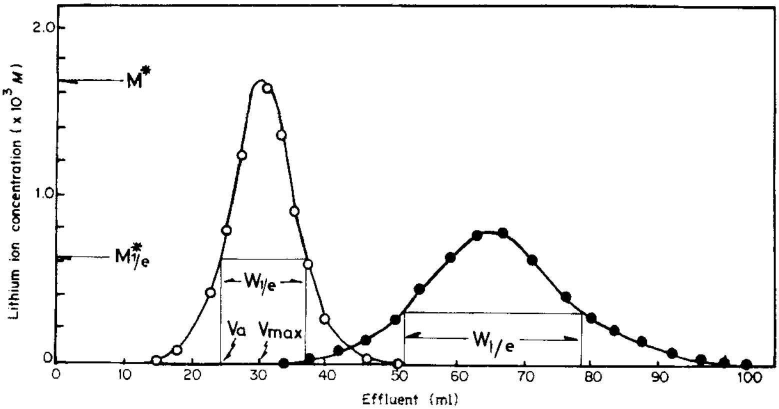

FIG. 1. Elution curves of lithium ions on C-SbA with nitric acid solution at different concentrations. C-SbA column, 6.0 × 0.8 cm i.d.; flow rate, mL/min; lithium ion loading, 0.01 mmole each. Concentration of nitric acid solution: (○) 0.005 M; (●) 0.003 M.

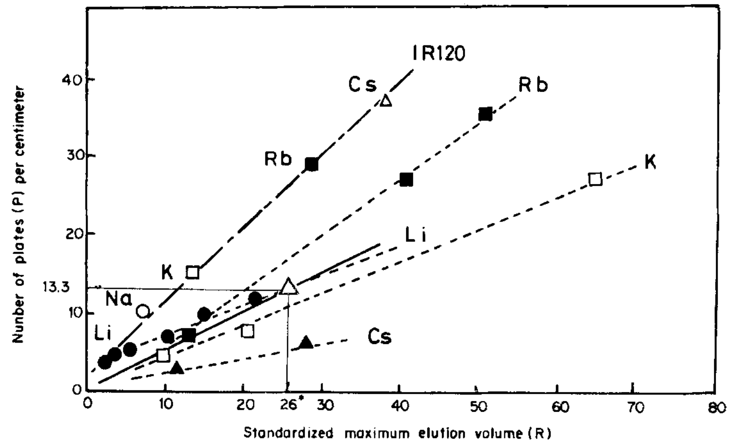

FIG. 2. Evaluation of number of plates per centimeter in HAP column. — - —: Amberlite IR 120; - -: C-SbA; $26^* = 30/3.0 \times (0.35)^2\pi$.

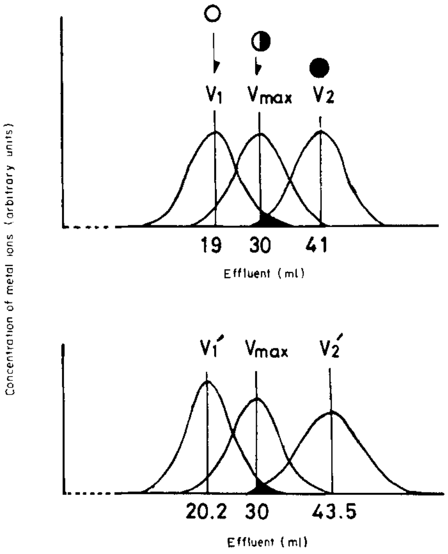

FIG. 3. Evaluation of maximum elution volume for different cases of elution. Case I (top): p is independent of the maximum elution volume. Case II (bottom): p depends on the maximum elution volume. (○) 97% eluted; (◑) half retained; (●) 99% retained.

curves of 97 % eluted, half, and 77 % retained are illustrated in Fig. 3 (top). Therefore

$$V_1 = V_{\max}\left\{1 - 1.88\frac{C}{p(C+1)}\right\} \tag{4a}$$

$$V_2 = V_{\max}\left\{1 + 2.33\frac{C}{p(C+1)}\right\} \tag{4b}$$

The corresponding values of 1.88 and 2.33 can be found in a table of probability integrals of 97 and 99 %, respectively. As mentioned above, the values of p depend on the $V_{\max}$ and the width of the elution band. The elution curves in such a case are illustrated in Fig. 3 (bottom). The values of V_1' and V_2' were determined as 20.2 and 43.5 by the try and error method by using Eqs. (4a) and (4b). Thus the K_d values of $K_{d(1)} = 19.8$ and $K_{d(2)} = 43.1$ were evaluated from the values of V_1' and V_2' by using Eq. (1). The K_d values evaluated by this treatment are shown with the equilibrium K_d values on C-SbA in Fig. 4.

Comparison of the Selectivities on C-SbA and HAP for Various Metal Ions (Fig. 4)

Alkali Metal Ions. Based on the determination of equilibrated K_d values, C-SbA exhibits the following selectivity sequence: $Li^+ < K^+ < Cs^+ < Rb^+ \ll Na^+$. For HAP: $Cs^+ < K^+, Rb^+ < Na^+$.

The estimated results of K_d values for Na^+ and Rb^+ on HAP agree well with those of equilibrated K_d values on C-SbA. The K_d values of Cs^+ on HAP can be regarded as identical to that on C-SbA by considering the difference between the dynamic conditions on the former exchanger and the equilibrium state on the latter exchanger. However, a disagreement of the K_d value of K^+ was observed between C-SbA and HAP, although C-SbA shows a reasonable rate of sorption and desorption for K^+. The marked difference in the preparation of two exchangers is the procedure in which the hydrolyzed precipitate is aged in the mother solution at 30 to 40°C for over 10 days in the case of C-SbA and is dried at 270°C for 5 hr in the case of HAP. Our previous report (*19*) revealed that the selectivity sequence did not vary with the thermal treatment of C-SbA in a temperature range of 25 to 330°C for 4 hr, although increased K_d values were observed after heating.

Alkaline Earth Metals. C-SbA exhibits the following selectivity sequence: $Mg^{2+} \ll Ba^{2+} < Ca^{2+} < Sr^{2+}$. For HAP: $Ca^{2+} < Ba^{2+} < Sr^{2+}$.

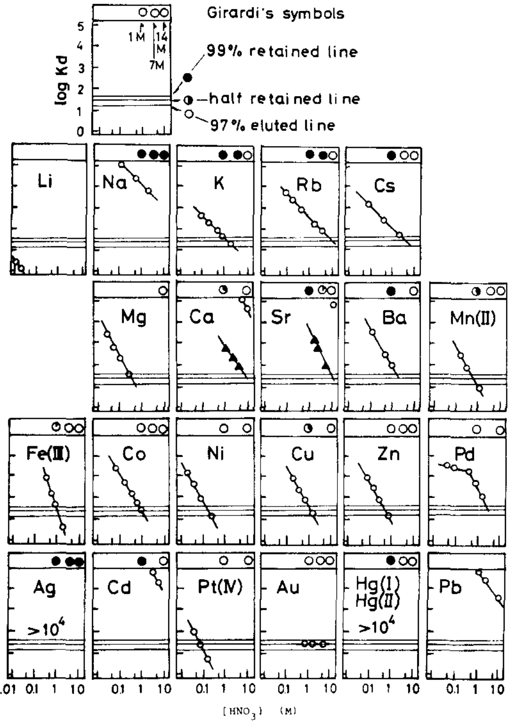

FIG. 4. Comparison between the equilibrated K_d values on C-SbA and the evaluated K_d values on HAP. (○) equilibrated K_d; (▲) K_d value after 24 hr.

An extremely slow rate for the ion-exchange reaction was observed on Ca^{2+}–H^+ and Sr^{2+}–H^+ systems studied earlier (*14*). It is evident that decreased K_d values were observed in the column experiments on HAP. Thus disagreement in the results with two exchangers may be explained in terms of the slow rates of adsorption and desorption for Ca^{2+} and Sr^{2+}.

Transition Metals. C-SbA exhibits the following selectivity sequence (*15*): $Ni^{2+} < Mn^{2+} < Zn^{2+} < Co^{2+} < Cu^{2+} < Cd^{2+}$. A slightly different sequence on the HAP column was reported (*11*): Ni^{2+}, Co^{2+}, $Zn^{2+} < Mn^{2+}$, $Cu^{2+} < Cd^{2+}$.

The evaluated K_d values for HAP are in very good agreement with those on C-SbA for the transition metals studied, except in the case of Cd^{2+}. C-SbA exhibits a much higher K_d value for Cd^{2+} than on HAP with a reasonable rate of adsorption.

Noble Metals. The evaluated K_d values for noble metals on HAP are in good agreement with those on C-SbA, except for Hg(II) and Pd(IV).

In conclusion, the retention data reported by Girardi et al. were analyzed for HAP columns on the basis of the extended plate theory. The results indicate that the ion-exchange selectivity in C-SbA is essentially compatible with that in HAP for 17 of 20 metal ions.

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