Synthetic Inorganic Ion-exchange Materials. XX. Ion-exchange Properties of Crystalline Antimonic(V) Acid with Alkaline Earth Metal Ions

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A stoichiometrical ion-exchange was observed for all the systems of Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} with H^+ in the crystalline antimonic(V) acid as a cation exchanger. The selectivity sequence, $Mg^{2+}<Ba^{2+}<Sr^{2+}<Ca^{2+}$, has been found for the ion-exchange reactions in 0.1 M nitrate salt solutions of different alkaline earth metals. Breakthrough and further elution studies were carried out in order to test the reversibility of the ion-exchange reactions. X-Ray analysis indicates that a solid solution forms for the ion-exchange system of the alkaline earth metal ions in the crystalline antimonic(V) acid.

Antimonic acid, $Sb_2O_5 \cdot 4H_2O$, has been of interest during last two decades because of its high ion-exchange capacity.[1] Various antimonic acid materials have been obtained with different chemical compositions and ion-exchange properties, depending on the method of preparation as well as on aging.[2] The species can be classified into three groups-crystalline, amorphous, and glassy. Among three different antimonic acids, crystalline antimonic(V) acid, C-SbA, shows an unusual selectivity for alkali metal ions as compared with the strong acid-type cation-exchange resins. The increasing selectivity shows: $Li^+<K^+<Cs^+<Rb^+<Na^+$ for microquantities of alkali metal ions in a nitric acid solution.[3,4] Similar unusual selectivity has been observed for polyantimonic acid[5] and hydrated antimony pentoxide.[6] These materials can be applied to the effective separation of sodium ion from certain elements.[3,4,6,7]

An unusual selectivity has been found in the ion-exchange system for microquantities of alkaline earth metal ions in a nitric acid solution.[8] An increasing order of selectivity is: $Mg^{2+}<Ba^{2+}<Ca^{2+}<Sr^{2+}$. A large difference in the distribution coefficients has been observed for the pairs of Mg^{2+}-Ba^{2+}, Ba^{2+}-Sr^{2+}, and Cs^+-Sr^{2+}. Effective separations can be achieved for these pairs.[8] Slightly different selectivities have been found for polyantimonic acid (PAA): $Mg^{2+}<Ca^{2+}<Sr^{2+}<Ba^{2+}$.[9]

In general, the selectivities of the inorganic ion-exchangers vary not only with the solution media, but also with exchange loading as a function of the concentration of the elements.

In this paper, the ion-exchange properties of C-SbA with macroquantities of alkaline earth metal ions will be reported.

Experimental

Reagents. The antimony pentachloride (Yotsuhata Chemical Co., Ltd.) was used without further purification. The other reagents used were all of an analytical grade.

Preparation of C-SbA as an Ion-exchange Material. C-SbA was prepared as has been described previously:[2] the precipitate obtained by the hydrolysis of antimony pentachloride was kept in the mother solution at 40 °C for over 20 days, and then washed with cold demineralized water with the aid of a centrifuge (about 10000 rpm) until it was free from chloride ions. After drying, the product was ground and sieved (100—200 mesh size). The collected sample was rewashed with demineralized water in order to obtain a clear supernatant solution following batch equilibrium experiments and to improve the elution-flow rate.

The Stoichiometry of Ion-exchange. Equilibrations were carried out by the batch technique as follows: a 0.25 g portion of the C-SbA was immersed in 25 ml of a 0.1 M nitrate salt solution of different alkaline earth metals at 30 ± 0.1 °C with intermittent shaking. The amounts of metal ions adsorbed were determined from the changes in the concentrations of the alkaline earth metal ions and hydrogen ions relative to the initial concentration of the solution after equilibration. The emf titration method was employed for determining the hydrogen-ion concentration by means of a standard sodium hydroxide solution.

Breakthrough Curves. A column, 2.3 long and 0.4 cm i.d., containing 0.40 g of C-SbA in hydrogen ion-form, was employed, with a flow rate of 0.3 ml/min. The concentrations of hydrogen ions liberated by the ion-exchange reaction were titrated with a standard sodium hydroxide solution, using methyl red as an indicator.

Elution Curves of Alkaline Earth Metal Ions. A nitric acid solution at different concentrations was passed through the C-SbA column saturated with alkaline earth metal ions with a flow rate of about 0.3 ml/min.

Composition of the Ion-exchanged C-SbA with Different Alkaline Earth Metal Ions. The ion-exchanged C-SbA of a weighed amount (0.1 g) was dissolved by heating in a mixed solution of 25 ml of a 12 M HCl solution and 10 ml of a 0.5 M KI solution. After cooling, a 10 ml portion of a 10% tartaric acid solution was added in order to avoid the hydrolysis of Sb(III) and a 50 mg portion of L-ascorbic acid was added to reduce of the I_3^- formed as a result of the reaction of oxidation-reduction from Sb(V) to Sb(III). The concentrations of the alkaline earth metals and of antimony in the solutions were determined by using a Varian-Techtron 1100 atomic-absorption spectrometer. The water content of the ion-exchanged C-SbA was calculated by subtracting the weights of the corresponding metal oxides from the initial weight.

X-Ray Power-diffraction Analysis. The X-ray data for the ion-exchanged C-SbA were determined by using a JEOL X-ray diffraction meter Model, JDX-7E with, Ni-filtered Cu $K\alpha$ radiation.

Results and Discussion

The results of the TGA, DTA, and X-ray studies of C-SbA in the hydrogen-ion form showed a good

Table 1. Stoichiometry of the ion-exchange reaction of alkaline earth metal ions on C-SbA

Ion-exchange system	Amounts meq/g			
	Mg^{2+}/H^+	Ca^{2+}/H^+	Sr^{2+}/H^+	Ba^{2+}/H^+
Adsorbed metal ions	0.61±0.02	3.37±0.02	3.15±0.02	2.55±0.02
Liberated hydrogen ions	0.60±0.05	3.40±0.05	3.10±0.02	2.50±0.05

agreement with our earlier works.[2,10)]

Batch Equilibration. The equilibrium for macroquantities of alkaline earth metal ions was attained within 3 months from our preliminary studies. For microquantities of Ca^{2+} and Sr^{2+}, previous work indicated that the exchange equilibrium would be attained in about 6 months. These phenomena may be explained by the presence of limited numbers of sites favorable to Ca^{2+} and Sr^{2+} making for a very tight network structure of the C-SbA. Thus no difference in the adsorbed amounts was observed within the limits of experimental error, although a further uptake of very small amounts occurred for a few consecutive months.

The relation between the liberated hydrogen ions and the adsorbed alkaline earth metal ions indicates a stoichiometry of the ion-exchange reaction for the systems studied (Table 1). The affinity sequence for macroquantities was found to be in this increasing order:

$$Mg^{2+} < Ba^{2+} < Sr^{2+} < Ca^{2+}$$

which was slightly different from the sequence for microquantities presented above. This may suggest that the selectivity sequence varys with the loading of the alkaline earth metal ions in C-SbA, as has been found for the ion-exchange systems of alkali metal ions–hydrogen ions on the C-SbA.[10)] A definite selectivity sequence has been reported for both micro- and macroquantities of the same system on PAA by Baetsle and Huys.[5)] However, no equilibrium time required has been reported in the literature. The rate of the adsorption of Ca^{2+} and Sr^{2+} was extremely slow, and the same sequence observed on PAA was found at the initial stage of the adsorption within a few weeks.

Breakthrough Curves. The breakthrough curves showed that hydrogen ions are liberated quantitatively for the equivalent uptake of alkaline earth metal ions by the ion-exchange reaction. The elution of the hydrogen ions by the ion-exchange proceeded rapidly at first, but they were still being liberated even after the passage of a relatively large volume of a 0.05 M nitrate salt solution of different alkaline earth metals, except in the case of the 0.05 M $Ba(NO_3)_2$ solution (Fig. 1). The breakthrough curve obtained for Ba^{2+}/H^+ exchange was steeper than those obtained for other systems. This can be explained by the fast rate of the adsorption for Ba^{2+} and the slow rate for the other alkaline earth metal ions, as was to be expected from a previous report.[8)] The breakthrough capacities were determined by the analysis of alkaline earth metal and antimony after decomposing the exchanged C-SbA, because the determination from the liberated hydrogen ions may lead to large experimental error because of long tailing.

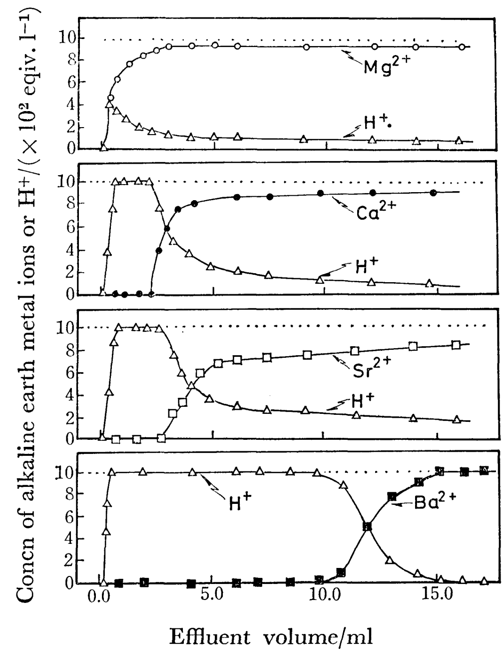

Fig. 1. Breakthrough curves for 0.05 M alkaline earth metal nitrate on C-SbA.
Column: 2.3×0.4 cm i.d., flow rate: 0.3 ml/min, —○—: Mg^{2+}, —●—: Ca^{2+}, —□—: Sr^{2+}, —■—: Ba^{2+}, —△—: H^+.

Elution of the Alkaline Earth Metal Ions Adsorbed on the C-SbA. Individual elution peaks with a sharp front and a tailing rear were observed for the elution of Mg^{2+}, Ca^{2+}, and Sr^{2+} (Figs. 2 and 3). Incomplete regenerations were achieved for the systems of Ca^{2+}/H^+ and Sr^{2+}/H^+, even if a 10 M nitric acid was used as an eluant. These phenomena may be due to the slow rate of desorption and the highly adsorptive ability on the C-SbA for Ca^{2+} and Sr^{2+}.

The adsorbed Ba^{2+} were eluted easily with a relatively small volume of a 1 M HNO_3 as an eluant. The results of the breakthrough and the elution are summarized in Table 2. The breakthrough capacities are found to be in the following increased order: $Mg^{2+}<Ca^{2+}<Ba^{2+}<Sr^{2+}$. The lower value of the breakthrough capacity than the uptake by batch equilibration for Ca^{2+} may be due to the slow rate of adsorption. A complete regeneration was achieved for the Ba^{2+}-exchanged C-SbA. Elutions of 79%, 31% and 43% for the adsorbed metal ions were achieved for Mg^{2+}, Ca^{2+} and Sr^{2+} respectively under the above experimental conditions.

The water contents of the C-SbA exchanged by

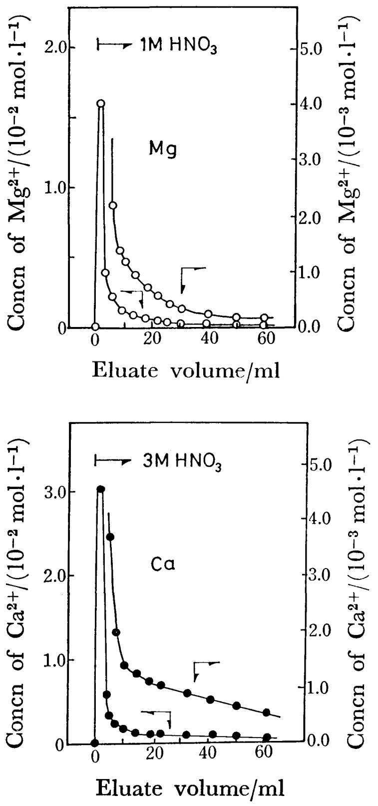

Fig. 2. Elution curves of Mg^{2+} and Ca^{2+} from the ion-exchanged C-SbA.
Column: 2.3×0.4 cm i.d., flow rate: 0.3 ml/min.

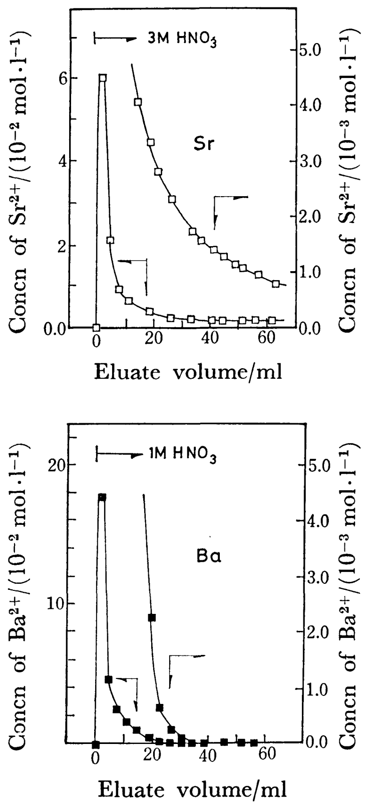

Fig. 3. Elution curves of Sr^{2+} and Ba^{2+} from the ion-exchanged C-SbA.
Column: 2.3×0.4 cm i.d., flow rate: 0.3 ml/min.

Table 2. Preparation and composition of the ion-exchanged C-SbA with different alkaline earth metal ions

Batch No.	Ion-exchange reaction	Influent[c]		M^{2+} Adsorbed (meq/g)[a]	Mole ratio in the exchanger	
		Breakthrough with	Elution with		MO/Sb_2O_5	H_2O/Sb_2O_5
1	$H^+ \rightarrow Mg^{2+}$	40 ml of 0.05 M $Mg(NO_3)_2$		0.53[b]	0.105	2.01
2	$Mg^{2+} \rightarrow H^+$	40 ml of 0.05 M $Mg(NO_3)_2$	70 ml of 1 M HNO_3	0.095	0.019	2.83
3	$H^+ \rightarrow Ca^{2+}$	800 ml of 0.05 M $Ca(NO_3)_2$		2.61[b]	0.516	1.47
4	$Ca^{2+} \rightarrow H^+$	800 ml of 0.05 M $Ca(NO_3)_2$	1500 ml of 3 M HNO_3 and 300 ml of 10 M HNO_3	1.81	0.358	1.85
5	$H^+ \rightarrow Sr^{2+}$	1000 ml of 0.05 M $Sr(NO_3)_2$		3.31[b]	0.654	0.726
6	$Sr^{2+} \rightarrow H^+$	1000 ml of 0.05 M $Sr(NO_3)_2$	1500 ml of 3 M HNO_3 and 300 ml of 10 M HNO_3	1.90	0.375	1.04
7	$H^+ \rightarrow Ba^{2+}$	30 ml of 0.05 M $Ba(NO_3)_2$		3.00[b]	0.594	3.35
8	$Ba^{2+} \rightarrow H^+$	30 ml of 0.05 M HNO_3	60 ml of 1 M HNO_3	0.0	0.0	4.47

a) meq/g of $Sb_2O_5 \cdot 4H_2O$. b) Breakthrough capacity. c) M: mol·l⁻¹.

Table 3. X-Ray diffraction data of the C-SbA exchanged by different alkaline earth metal ions

Batch No. Exchanged	H$^+$		1 Mg^{2+}		3 Ca^{2+}		5 Sr^{2+}		7 Ba^{2+}	
hkl	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
111	5.993	100	6.00_2	100	5.914	85	5.973	59	6.010	50
311	3.131	76	3.134	79	3.091	70	3.120	40	3.139	42
222	2.998	78	3.001	74	2.961	100	2.986	100	3.005	100
400	2.596	15	2.599	17	2.564	18	2.587	19	2.602_5	22
331	2.382	10	2.386	11	2.352	6	2.373	5		
422	2.119	4	2.124_5	1						
511	1.998_5	22	2.001_4	18	1.973_8	19	1.991	11	2.004	11
440	1.835_3	35	1.837_0	34	1.813_1	45	1.828_4	38	1.840_5	34
531	1.755	23	1.756_8	20	1.733_6	18	1.749_1	10	1.759_0	13
533	1.582_9	11	1.585_1	6	1.564_1	9	1.577_4	6	1.587_3	7
622	1.565_2	28	1.566_9	27	1.546_1	31	1.559_2	27	1.569_1	30
444	1.499_4	6	1.500_7	6	1.480_5	8	1.493_3	5	1.502_4	7
711	1.453_9	18	1.455_6	12	1.436_3	10	1.447_9	6	1.457_6	10
731	1.351_3	11	1.353_7	9	1.336_4	12	1.347_4	8	1.355_9	8
$\bar{a}$(Å)	10.38_2		10.39_6		10.25_7		10.34_6		10.40_9	

$\bar{a}$: Mean lattice constant.

different alkaline earth metal ions decrease with an increase in the amounts of the metal ions adsorbed and also with an increase in the crystal ionic radii of the metals, except in the case of Ba^{2+}. This indicates that the net transfer of some water molecules from the solid phase to the solution phase occurs with the ion-exchange of the alkaline earth metal ions on the C-SbA in hydrogen-ion form.

X-Ray Analysis. The X-ray diffraction data of the ion-exchanged C-SbA with different alkaline earth metal ions are summarized in Table 3.

There are changes in the lattice constant of up to a few percent with the cations adsorbed, but no change in the space group, Fd3m. Similar behavior is established for C-SbA and various zeolites on the ion-exchange systems of the alkali metal ions.[10,11] This may be due to the fact that C-SbA does not undergo remarkably any dimensional change with the ion-exchange because of its three-dimensional framework structure, like that of zeolite. In contrast, clay mineral and crystalline zirconium phosphate, possessing two dimensional structure, may undergo swelling or shrinking and may also be converted to two immiscible phases during the ion-exchange of some metal ions.[11,12] All of the X-ray diffraction patterns determined belong to Fd3m, and no immiscible phase was found over the entire range of systems studied. A remarkable decrease in the diffraction intensities of the (111) and (311) planes was observed with an increase in the crystal ionic radii of the adsorbed metal ions, while the (222) plane increased.

The calculated values of the lattice constant of the ion-exchanged C-SbA are plotted against the effective ionic radii of the metal ions in Fig. 4, the data of the C-SbA exchanged with alkali metal ions being included for comparison. The effective ionic radii can be found from the Shannon and Prewitt Table by assuming that the metal ion has six-coordinated radii.[13] A strong dependence on the effective ionic radii was noticed for the changes in the lattice constant, although it may be very difficult to explain its relationship quantitatively because of the metal ions adsorbed in different amounts in the C-SbA. When the exchanging cation, Na$^+$ or Ca^{2+}, has an ionic radii of about 1.0 Å, the lattice constant decreases markedly, as compared with that of the C-SbA in the hydrogen-ion form. Increased lattice constants are observed for the adsorption of a metal ion with effective ionic radii of about 1.3 Å (in the case of K$^+$ and Ba^{2+}).

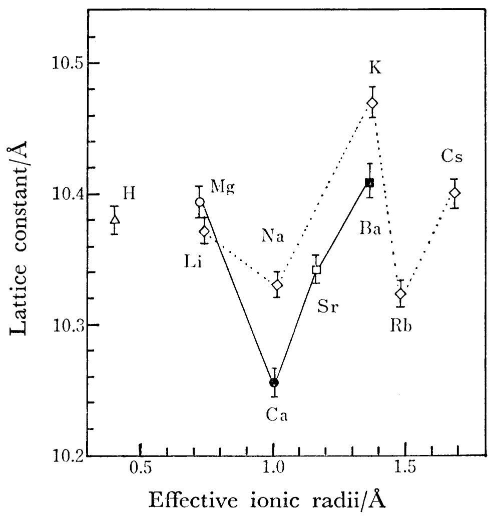

Fig. 4. Changes in the lattice constant of the C-SbA ion-exchanged with alkaline earth metal ions.
△: H-form, ○: (1), ●: (3), □: (5), ■: (7), A numeral in parenthesis indicates batch number.

Our work indicates that C-SbA has interstitial-(free) water with the chemically bonded water combined as Sb–OH.[14] The shrinking of the crystal lattice makes it progressively easier to exclude some

Table 4. X-Ray diffraction data of the ion-exchanged C-SbA samples after regeneration with nitric acid solutions as eluants

Batch No. Exchanged	2 $Mg^{2+} \rightarrow H^+$		4 $Ca^{2+} \rightarrow H^+$		6 $Sr^{2+} \rightarrow H^+$		8 $Ba^{2+} \rightarrow H^+$	
hkl	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
111	6.001	100	5.953	100	5.981	85	5.993	100
311	3.134	67	3.104	82	3.121	61	3.130	58
222	2.999	77	2.973	95	2.987	100	2.995	70
400	2.598	15	2.574	16	2.588	23	2.594_5	14
331	2.384	10	2.362	8	2.374	7	2.381	10
422	2.122	4					2.118	2
511	1.996	14	1.981_5	20	1.991_4	18	1.997_2	17
440	1.836_3	20	1.819_9	44	1.828_7	38	1.834_3	28
531	1.755_8	22	1.740_6	20	1.749_3	17	1.753_9	21
533	1.583_8	6	1.570_4	12	1.577_4	4	1.582_4	9
622	1.566_4	20	1.552_0	33	1.560_1	33	1.564_0	24
444	1.499_2	4	1.486_2	6	1.493_5	8	1.498_3	6
711	1.454_8	13	1.441_4	9	1.449_3	10	1.452_7	12
731	1.352_9	9	1.340_5	12	1.347_5	9	1.351_2	13
$\bar{a}$(Å)	10.38_8		10.29_6		10.34_9		10.37_8	

$\bar{a}$: Mean lattice constant.

of the water molecules of the solid phase by the ion-exchanging metal ions. In contrast, the swelling may cause some of the water molecules to be retained with the exchanging metal ions. If the dimension of the crystal lattice remain constant during the ion-exchange, the net transfer of some of the water molecules from the solid phase to the solution phase are probably caused by the adsorption of the metal ion with large effective ionic radii. The differences in the water content in the C-SbA exchanged with Ba^{2+} and with Ca^{2+} can be explained by the swelling and the shrinking.

The X-ray diffraction data of the C-SbA regenerated by different nitric acid solutions are summarized in Table 4. The X-ray data for the regenerated sample (Batch No.8) show that the conversion from the Ba^{2+}-exchanged C-SbA to the C-SbA in the hydrogen-ion form is indeed reversible within the limit of experimental error. In the other system, the X-ray patterns show intermediate profiles between the fully exchanged C-SbA and the C-SbA in hydrogen-ion form in the diffraction intensities and in values of the lattice constant.

The apparent irreversibility for the ion-exchange systems of Ca^{2+}/H^+ and Sr^{2+}/H^+ may be due to the extremely slow rate of adsorption and desorption in addition to the extremely high adsorptive ability of C-SbA for Ca^{2+} and Sr^{2+}.

Only a single phase is noticed over the entire range of C-SbA ion-exchanged with different alkaline earth metal ions. This indicates that a solid solution forms for the ion-exchange system of the metal ions in the C-SbA.

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