Synthetic Inorganic Ion-exchange Materials. XXVI. Ion-exchange Properties of Crystalline Antimonic(V) Acid towards Noble Metals in Nitric Acid Media

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A study of the distribution coefficients on crystalline antimonic(V) acid (C-SbA) shows an unusual affinity series {Pt(IV) < Au(III) < Pd(II) ≪ Hg(I), Hg(II), Ag(I)} for microamounts of noble metal ions in nitric acid solution, as compared with ion-exchange resins in strong acid type. Extremely high adsorptive properties are found on the exchange system of Hg(II) and Ag(I), even in relatively high concentrations of nitric acid solution. The ion-exchange studies for macroamounts indicate that a solid solution forms for the system of the Ag(I) ions and hydrogen ions in C-SbA, while two solid phases are presented for the system of Hg(II) ions and hydrogen ions.

There has been a large amount of research on synthetic inorganic ion-exchange materials because of their thermal stability and resistance to radiation, and high selectivities for certain elements.[1–6]

Among these inorganic ion-exchangers, crystalline antimonic(V) acid (C-SbA) has been of interest in the last decade due to its high cation-exchange capacity and high selectivities for certain elements.[7–10] The increasing order of selectivities for microquantities show; $Li^+ < K^+ < Cs^+ < Rb^+ < Na^+$ for alkali metals,[8,10] $Mg^{2+} < Ba^{2+} < Ca^{2+} < Sr^{2+}$ for alkaline earth metals,[11] and $Ni^{2+} < Mn^{2+} < Zn^{2+} < Co^{2+} < Cu^{2+} < Cd^{2+}$ for transition metals[12] in nitric acid media. Extremely high absorptive ability was found for Na^+, Ca^{2+}, Sr^{2+}, and Cd^{2+} on C-SbA. The large differences in the distribution coefficients have been observed for several pairs of the elements. Some mutual separations can be achieved effectively for alkali metals,[8,10,13] Mg^{2+}–Ba^{2+}, Ba^{2+}–Sr^{2+}, Cs^+–Sr^{2+},[11] Ni^{2+}–Zn^{2+}, and Zn^{2+}–Cd^{2+} pairs[12] by using a relatively small C-SbA column.

Similar compounds to C-SbA have been reported, *e.g.* polyantimonic acid (PAA) by Lefebrve *et. al.*[14,15] and Baetsle and Huys,[16] and hydrated antimony pentoxide (HAP) by Girardi *et al.*[17]

This paper describes the ion-exchange properties of C-SbA for noble metal ions.

Experimental

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

A solution of Ag(I), Hg(I), and Pd(II) was prepared by dissolving the corresponding nitrate salts with water and a solution of Hg(II) was prepared by dissolving the nitrate salt in 0.1 M (1 M = 1 mol dm^{-3}) nitric acid solution in order to prevent hydrolysis of Hg^{2+}. Tetrachloroauric(III) acid and hexachloroplatinic(IV) acid were used for preparing the solutions of Au(III) and Pt(IV).

Preparation of C-SbA as an Ion-exchange Material. C-SbA was prepared as described previously:[10,11] the precipitate obtained by the hydrolysis of antimony pentachloride was kept in the mother solution at 40 °C for more than 20 d. The precipitate was washed with cold demineralized water in a centrifuge (10000 rpm) until free from chloride ions, dried and the product 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.

Distribution Coefficients (K_d). The values for K_d for the noble metal ions were determined by batch operation as follows. C-SbA (0.250 g) was immersed in nitric acid solution (25.0 cm^3) containing 1×10^{-4} M of the metal ions at 30±0.1 °C with occasional shaking. The amount of metal ions adsorbed was determined from the changes in the concentration of the metal ions relative to the initial concentrations of the solution after equilibration. The concentrations of the metal ions were determined spectrometrically with *p*-diethylaminobenzalrhodanine for Ag(I), Hg(I), Hg(II), and Au(III), with tin(II) chloride for Pt(IV) and with sodium iodide and sodium sulfite for Pd(II).[18,19] The emf titration method was employed for determining the hydrogen ion concentration by means of a standardized sodium hydroxide solution.

Preparation of the Ion-exchanged C-SbA. The C-SbA ion-exchanged with Ag(I) in different degree was prepared by immersing C-SbA in 0.1 M $AgNO_3$ solution of which the volume contained amounts corresponding to 25, 50, or 80% of its theoretical capacity. The theoretical capacity (5.06 meq/g) may be estimated from the empirical formula $Sb_2O_5 \cdot 4H_2O$ assuming that one antimony atom gives one hydrogen ion available for ion-exchange.[20] In the case of C-SbA ion-exchanged with Hg(II), a solution containing 0.05 M $Hg(NO_3)_2$ in 0.1 M nitric acid solution was used. The fully ion-exchanged C-SbA with Ag(I) and Hg(II) was prepared by a breakthrough experiment as follows; a 0.1 M $AgNO_3$ was passed continuously through the C-SbA column of 0.5 g with a flow rate of 0.3 cm^3/min, and a 0.05 M $Hg(NO_3)_2$ solution containing 0.1 M HNO_3 was used for the fully ion-exchanged C-SbA. Injection was continued until the change in the concentration of metal ions between influent and effluent was negligible within the experimental error.

X-Ray Diffraction Analysis. The X-ray diffractions for the ion-exchanged C-SbA were determined using a JEOL X-ray Diffractometer Model, JDX-7E, with Ni-filtered Cu*Kα* radiation.

Results and Discussion

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

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agreement with earlier data.[10,20]

Adsorption of Noble Metal Ions. The time dependence on the adsorption of different metals was measured qualitatively in order to determine the equilibrium distribution coefficients (Fig. 1). Equilibrium was attained within 3, 4, and 7 d for Pd(II), Au(III), and Pt(IV) respectively. Complete adsorption (99—100%) was achieved for Ag(I), Hg(I), and Hg(II) within 24 h.

Distribution Coefficients. The equilibrium distribution coefficients of noble metal ions on C-SbA are shown in Fig. 2 as log-log plots of K_d *vs.* $[HNO_3]$. The slope, d log K_d/d log $[HNO_3]$, for the Pd(II)–H^+ system is approximately 2 in the concentration range 0.5—2 M HNO_3 and approximately 1 in the range 0.05—0.5 M. Similar behavior has been found on Dowex 50W-X8, indicating the "ideal 2:1 ion-exchange reaction" of Pd^{2+}/H^+ at relatively high concentration of nitric acid solution. The reduction in slope may be explained in terms of the ion-exchange reaction of the $Pd(OH)^+$–H^+, since the $Pd(OH)^+$ species increases with decreasing concentration of hydrogen ions below 0.5 M HNO_3 from studies of the stability constant of the Pd(II)–OH^- system.[21] The slope was approximately 2 for the Pt(IV)–H^+ system, while the K_d value for Au(III) was independent of the concentration of nitric acid. It is known that in perchloric acid solution, the Pt(IV) ion is unaffected by cation-exchange resins such as Dowex 50, while in chloride solution the Pt(IV) ion gives stable chloride complexes which can be retained quantitatively by anion-exchange resins.[22] On the ion-exchange system in aqueous solution, cationic species of Pt(IV) can not be found in the literature known so far. It has been reported that chloride and nitrate ions are unaffected by antimonic(V) acid in most media, but that phosphate ions can be adsorbed in phosphoric acid solutions.[23] The adsorptive behavior of Pt(IV) and Au(III) may be due to a difference in mechanism in the cation-exchange reaction.

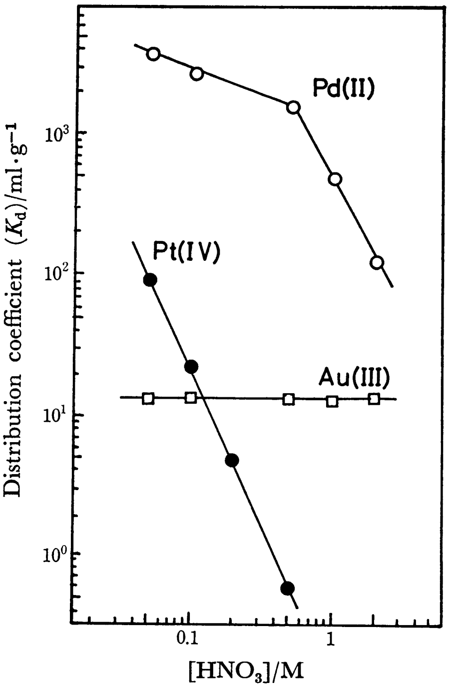

Fig. 2. Distribution coefficients of noble metals on C-SbA at different concentration of nitric acid solution. Initial concentration of the metals, $1.\times10^{-4}$ M. C-SbA, 0.250 g. Total volmue, 25.0 cm^3. Temperature, 30±0.1 °C.

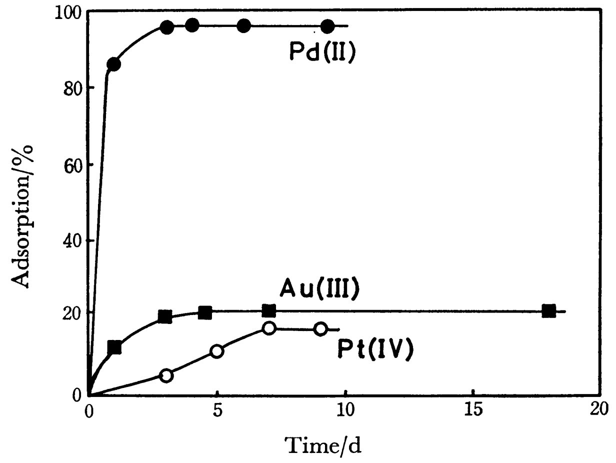

Fig. 1. Time dependence of the adsorption of noble metals on C-SbA in 0.2 M nitric acid solution. Initial concentration of metal ions, 1×10^{-4} M, C-SbA, 0.250 g. Total volume, 25.0 cm^3. Temperature, 30±0.1 °C.

The K_d values obtained are summarized in Table 1, the values on cation-exchange resin being included for comparison. The results obtained on Dowex 50W-X8 are in fairly good agreement with the results reported by Strelow *et al.*[24] Extremely high values of K_d($>10^4$) were observed for Ag(I), Hg(I), and Hg(II) on C-SbA in the concentration range 0.05—2 M HNO_3, compared with the ion-exchange resins. The following affinity series was found for C-SbA: Pt(IV)<Au(III)<Pd(II)≪Hg(I), Hg(II), Ag(I) in 0.5 M HNO_3 solution.

TABLE 1. DISTRIBUTION COEFFICIENTS FOR NOBLE METALS ON C-SbA IN 0.5 M HNO_3

Ion-exchanger	Pt(IV)	Au(III)	Pd(II)	Hg(I)	Hg(II)	Ag(I)
C-SbA	0.56	32	1.5×10^3	$>10^4$	$>10^4$	$>10^5$
	Pt(IV)	Ag(I)	Au(III)	Hg(II)	Hg(I)	Pd(II)
Dowex 50W-X8	—	35	2.1×10^2	3.2×10^2	7.2×10^2	1.4×10^3
BIO-RAD AG50W-X8[a)]	—	36.0	—	1.21×10^2	6.4×10^2	23.5

a) Data from Ref. 24.

Preparation of the Ion-exchanged C-SbA with Ag(I) and Hg(II). A solution containing Ag(I) or Hg(II) of macroamounts, corresponding to 25, 50, or 80% of the theoretical capacity when added to C-SbA, the liberated hydrogen ions were found to be equivalent to the metal ions added. This indicates that complete adsorption was achieved in both systems in the determination of metals and hydrogen ions within experimental error. In the batch system of Hg(II)–H+, especially a very small quantity ($\simeq 10^{-6}$ M) of Hg(II) was observed in the supernatant solution equilibrated with C-SbA.

The breakthrough curves show that hydrogen ions are liberated quantitatively for an equivalent uptake of Hg(II) and Ag(I) ions (Fig. 3). The curves obtained are steep, indicating a reasonable rate of ion-exchange for the metal ions. The breakthrough capacities were found to be 4.95 meq/g for Ag(I) and 5.06 meq/g for Hg(II), which are in good agreement with the theoretical capacity for C-SbA. A similar result for Ag(I) has been reported; 5.0 meq/g by Lefebrve and Gaymard[15] and 5.1±0.5 meq/g by Baetsle and Huys.[16] The color of the C-SbA in the H+ form changed from which to yellow on complete exchange of Ag(I) or Hg(II).

The addition of a 5 M nitric acid solution to the fully exchanged C-SbA with Hg(II) produced very small quantities ($\simeq 10^{-5}$ M) of Hg(II) which were found in the supernatant solution (50 cm^3).

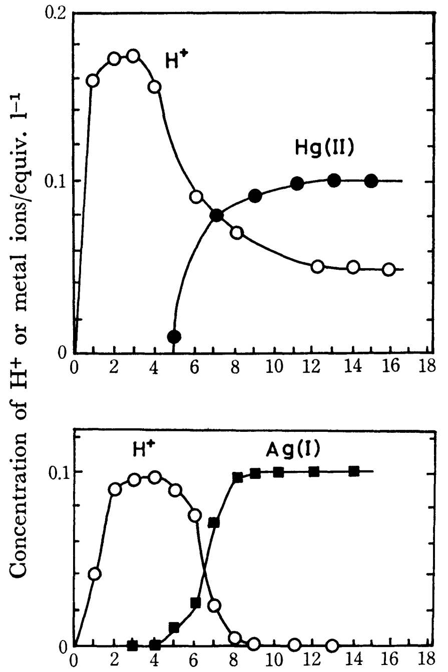

Fig. 3. Breakthrough curves for Hg(II) and Ag(I) on C-SbA. C-SbA column, 0.5 g. Flow rate, 0.3 cm^3/min.
Influent: Hg(II), 0.05 M Hg(NO$_3$)$_2$ in 0.1 M HNO$_3$, Ag(I); 0.1 M AgNO$_3$. -O-: H+, -●-: Hg(II), -■-: Ag(I).

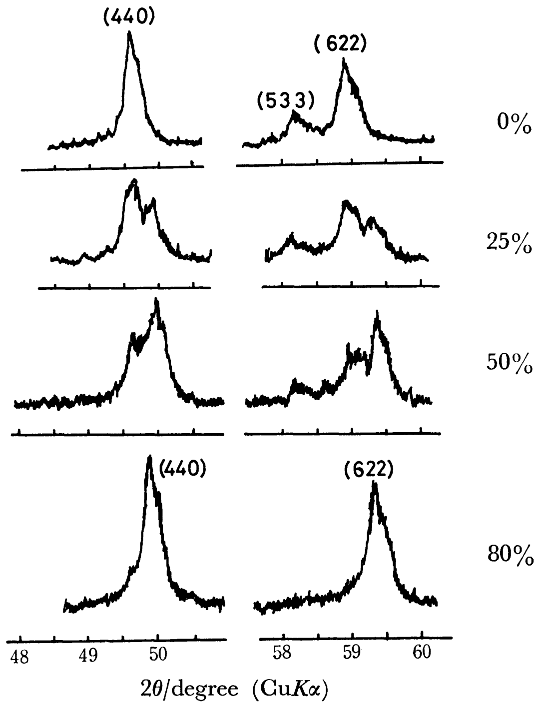

Fig. 4. Schmatic diagrams of X-ray diffraction patterns for (444), (533), and (622) planes of the C-SbA ion-exchanged with Hg(II) at different loading.

X-Ray Analysis. The X-ray diffraction patterns of the C-SbA ion-exchanged with Hg(II) revealed two solid phases present on the C-SbA exchanged by approximately 10—80%. Typical patterns *viz.* (440), (533), and (622) are illustrated in Fig. 4. Both phases belong to the crystal system of Fd3m with a lattice constant of 10.37_5 and 10.31_4 Å. The former phase may be identified as the unexchanged C-SbA in the H+ form. The diffraction intensities of the latter phase increase with increasing degree of ion-exchanging Hg(II) ions while those of the former decrease simultaneously. A single phase was observed for the C-SbA ion-exchanged by several metal ions, such as the alkali metals,[25] the alkaline earth metals,[26] and transition metals.[27] It has been established that the presence of two phases during ion-exchange is often observed in the system of ion-exchange on crystalline zirconium- or titanium-phosphate exchangers.[28–30] The presence of two solid phases is however the first case in the ion-exchange systems of C-SbA.

The calculated lattice constants for the C-SbA ion-exchanged with Hg(II) and Ag(I) are plotted against the loading of the ion-exchanging metal ions in Fig. 5. The lattice constants of the C-SbA ion-exchanged with Ag(I) decreased continuously with the degree of exchanging Ag(I) ions indicating that a solid solution forms for the ion-exchange system of the Ag+ and hydrogen ions in the C-SbA. The X-ray diffraction data for the fully ion-exchanged C-SbA with Ag(I) and Hg(II) ions are summarized in Table 2. A remarkable decrease on the diffraction intensities of the (111) and (311) planes was observed for both ion-exchanged C-SbA, while the (222) plane increased simultaneously. Similar behavior was observed on the C-SbA ion-exchanged with relatively heavy metal ions sucn as Ag+, Rb+, Cs+, Sr^{2+}, and Ba^{2+}.[25,26,31] Further ion-exchange studies Hg(II) with

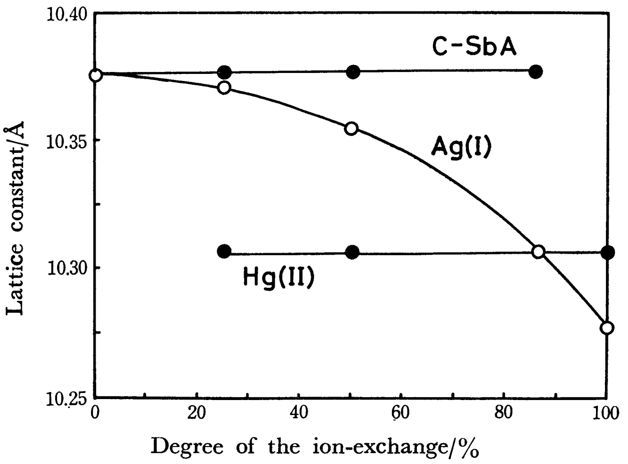

Fig. 5. Lattice constants as a function of the loading of the C-SbA ion-exchanged with Hg(II) or Ag(I). -○-: Ion-exchanged with Ag(I), -●-: ion-exchanged with Hg(II).

TABLE 2. X-RAY DIFFRACTION DATA OF THE C-SbA EXCHANGED WITH Ag(I) AND Hg(II)

Exchanged	H+		Ag(I)		Hg(II)	
hkl	d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0
111	5.970	100	5.953	2		
311	3.127	54	3.098	2		
222	2.995	62	2.964	100	2.977_5	100
400	2.594	13	2.567_9	40	2.579_0	34
331	2.377_9	11				
422	2.118_0	2				
333	1.995_6	16				
440	1.833_0	29	1.818_3	43	1.823_4	48
531	1.753_0	21	1.737_1	43		
533	1.582_4	9				
622	1.563_5	23	1.549_5	33	1.555_0	62
444	1.497_5	5	1.483_2	9	1.489_7	8
711	1.452_6	13	1.439_7	1		
713	1.350_6	10				
ā[a]	10.37_5		10.28_0		10.31_4	

a) ā: Mean lattice constant.

regard to irreversibility will be published at a later date.[32]

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