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SYNTHESIS OF QUADRIVALENT METAL ANTIMONATES AS ION EXCHANGERS AND THEIR SELECTIVITIES FOR ALKALI METAL IONS

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Various antimonates of quadrivalent metals were synthesized by hydrolysis of a mixed solution with antimony(V) chloride solution and a solution of quadrivalent metal salt. The equilibrium distribution coefficients for alkali metal ions on the samples prepared were determined for their selectivities.

The synthesis of inorganic ion-exchangers has been studied extensively by various workers.[1)] Excellent selectivities on the inorganic ion exchangers have been found for a certain element or group of elements in presence of a large amount of other bulk components.

Quadrivalent metal antimonates as ion-exchangers have been studied first by Abe and Ito.[2)] Especially, tin(IV) antimonate(SnSbA) behaves as a cation exchanger with relatively high capacity, and shows an excellent selectivity for alkali metal ions in the order: $Na < K < Rb < Cs << Li$,[3)] which is not included in Eisenman's selectivity series.[4)] It has been known that the ion exchange properties including its selectivity are much dependent on their preparative conditions. However, high selectivity for lithium ions can be expected among other quadrivalent metal antimonates prepared by a similar procedure to that of SnSbA, as is known for quadrivalent metal phosphate cation exchangers.[1)]

This paper describes synthesis of quadrivalent metal antimonate and their selectivities for alkali metal ions.

Various antimonates of quadrivalent metals were prepared in the following manner. A liquid antimony(V) chloride was prehydrolyzed with an equal amount of demineralized water. The 3.9 M($M = mol\ dm^{-3}$) antimony(V) chloride solution obtained was mixed in a quadrivalent metal salt solution with a molar ratio 1:1 on metal basis. The mixed solution was immediately hydrolyzed in demineralized water at 60 °C. The precipitate obtained was kept in the mother solution overnight, then was filtered and washed with water by using a centrifuge (10000 rpm). After drying at 60 °C, the product was ground and sieved(100-200 mesh size).

The products obtained were identified by X-ray powder diffraction analysis by using a JEOL X-ray diffractometer model JDX-7E, with Ni-filtered Cu-Kα radiation. The synthetic conditions and the results of X-ray analysis were summarized in Table 1. The X-ray analysis showed a weak diffraction pattern of rutile type and of almost amorphous form for the products obtained from titanium and zirconium salts, respectively. In the cases of colloidal silica and manganese salt, the products gave the X-ray patterns of crystalline antimonic(V) acid with a crystal system of Fd3m.

Table 1. The synthetic conditions and X-ray analysis.

Sample	3.9 M $SbCl_5$	quadrivalent metal salts	H_2O(cm^3)	X-ray analysis
A	21 cm^3	4.5 M $TiCl_4$, 19 cm^3	1000	Rutile type
B	8 cm^3	1 M $ZrOCl_2$, 32 cm^3	1000	Nearly amorph.
C	50 cm^3	1.2 M Colloidal SiO_2,150 cm^3		C-SbA[a)]
D	14 cm^3	0.4 M $KMnO_4$, 1000 cm^3		C-SbA & trace[b)]
(+2 M $MnSO_4$,23 cm^3)				

a) Crystalline antimonic(V) acid.
b) Very weak diffraction lines of unknown material.

The distribution coefficients(Kd) of alkali metal ions were determined by batch equilibration. A sample(0.25 g) was immersed in alkali metal chloride solution of 10^{-4} M(25 cm^3) containing different amount of hydrochloric acid. The concentration of alkali metal ions in the exchanger and in the solution was deduced from the concentration relative to the initial concentration in the solution. The concentrations of the alkali metal ions were determined by flame photometry or atomic absorption spectrometry. The Kd values were calculated as follows:

$$\mathrm{Kd} = \frac{\text{Amount of metal ions in exchanger}}{\text{Amount of metal ions in solution}} \times \frac{\text{cm}^3 \text{ of solution}}{\text{g of exchanger}}$$

The Kd values were compared at different concentrations of hydrochloric acid, because an intercomparison at the same acid concentration would introduce a large experimental error into the extrapolated values (Table 2).

Table 2. The Kd values of alkali metal ions and separation factors(α) on various samples

Sample	HCl(M)		Na		K		Rb		Li		Cs
A	0.01	Kd	46		510		1.6×10^3		2.1×10^3		8.8×10^3
		α		11		3.1		1.3		4.4	
B	0.0001	Kd	no adsorption(Kd ⩽ 1)								
			Li		Rb		Cs		K		Na (from elution expl.)
			Li		K		Rb		Cs		Na
C	1.0	Kd	< 1		15		110		170		2.4×10^3
		α		> 15		7.3		1.5		14	
D	0.3	Kd	32		190		4.1×10^3		5.4×10^3		1.9×10^4
		α		5.9		21		1.3		3.5	

The selectivity sequence on the samples C and D is similar to that of C-SbA.1) As mentioned above, the X-ray diffraction patterns on the samples C and D show presence of only C-SbA as a crystalline phase. It is obscure that silicon or manganese forms antimonates. These results indicate that the antimonates of silicon and manganese have less contribution for the selectivity of alkali metal ions, even if they were present in the sample. A very weak adsorption property was observed on the zirconium antimonate(sample B), which was in good agreement with that observed on our earlier study.2) The titanium antimonate(sample A) showed an unique order of selectivity: Na < K < Rb < Li < Cs. This unusual order is not

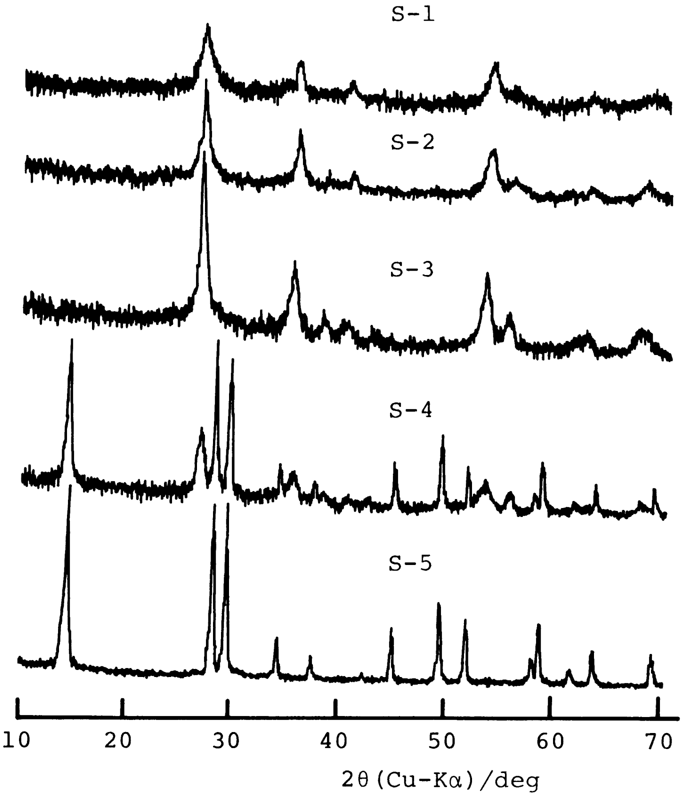

Fig.1. X-Ray Powder diffraction patterns of titanium antimonates prepared under different conditions.

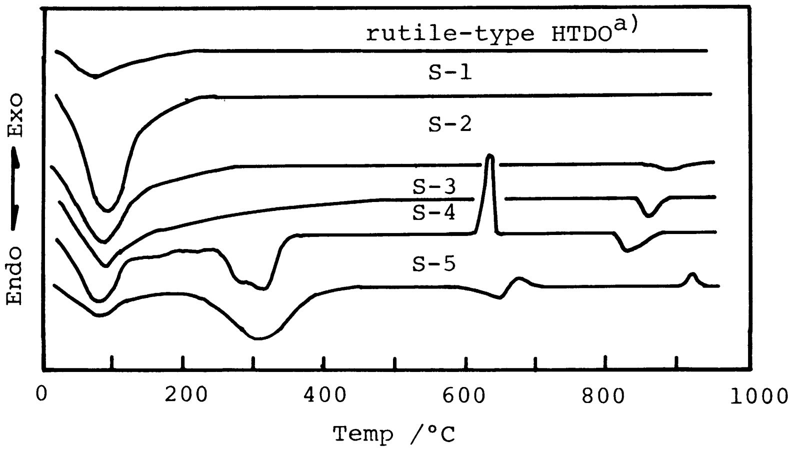

Fig.2. DTA Curves for titanium antimonates prepared under different conditions.
a) Hydrous titanium dioxide.

included in the 11 selectivity series predicted by Eisenman.[4] The selectivity order, except Li, is parallel to the increasing order of effective ionic radii for alkali metal ions. The separation factor calculated from the Kd values of lithium and sodium ions is a value of 46, which is much higher than those observed on commercial ion exchange resins.[5] This behavior is very good advantage for preferential adsorption of lithium ions from sodium ions. Further studies were carried out for the titanium antimonate(Ti-SbA) prepared by different conditions.

The Ti-SbA was precipitated by hydrolyzing a 40 cm^3 of a mixed solution of $SbCl_5$ and $TiCl_4$ with varying molar ratios(Ti/Sb) in the range of 0.25-4.0 into a 960 cm^3 of water at 60 °C. The precipitate obtained was washed with water by using a centrifuge(about 10000 rpm) until the pH value of supernatant solution was higher than 1.5. After drying at 60 °C, the product was ground and sieved(100-200 mesh size).

The X-ray diffraction patterns of the Ti-SbA for S-1(4.0 of Ti/Sb molar ratio), S-2(1.5) and S-3(1.0) showed the rutile type (Fig.1). A mixed pattern of the rutile type and C-SbA was observed for S-4(0.67), and the pattern of C-SbA for S-5(0.25). The crystallinity of the rutile type increased with decreasing the molar ratio of Ti/Sb upto 1.0.

The differential thermal analysis(DTA) for S-1, -2, and -3 showed similar pattern to the result obtained for hydrous titanium dioxide in rutile type(Fig.2). A mixed pattern of DTA curves observed for amorphous and crystalline antimonic acids was obtained for sample S-4. The DTA curve of S-5 showed similar pattern to that for C-SbA.[1] The results obtained on the X-ray analysis and DTA indicate that the S-4 contains amorphous antimonic acid and C-SbA and that the S-5 involves C-SbA. The crystal system of the S-1 to S-3 was essentially the same as that of TiO_2 in rutile type and no indication was observed for the presence of amorphous antimonic acid or C-SbA. The S-1 to S-3 showed about the same lattice parameters(a_o 4.67 Å and c_o 2.97 Å). They are larger than those of rutile-type hydrous titanium dioxide(a_o 4.61 Å, c_o 2.96 Å) prepared by hydrolysis of $TiCl_4$ at 60 °C. The tentative structure can be postulated as follows: the -OSbOH as a functional group is distributed homogeneously onto the TiO_2 matrix in rutile type by dehydrated condensation, as postulated for the SnSbA.[3]

The separation factors, α^{Li}_{Na} , on the Ti-SbA obtained at different preparations showed the values of 1, 46, 96, and 46 for the molar ratios(Ti/Sb) of 0.7, 1.0, 1.5 and 4.0, respectively. The maximum value(α^{Li}_{Na} = 96) was obtained around the molar ratio(Ti/Sb) of 1.5, which was 48 times higher than that observed on commercial organic ion-exchange resins in strong acid type.[5]

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