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SYNTHESIS AND IR, X-RAY AND ION-EXCHANGE STUDIES OF SOME AMORPHOUS AND SEMICRYSTALLINE PHASES OF TITANIUM ANTIMONATE

SEPARATION OF VO²⁺ FROM VARIOUS METAL IONS

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SUMMARY

Amorphous and semicrystalline samples of titanium antimonate have been synthesized by mixing solutions of titanium (IV) chloride and antimony pentachloride of different concentrations in various volume ratios at a constant pH of zero. The selectivities for twenty-seven metal ions of four chemically different samples have been compared. IR spectra and d values for titanium antimonates have been compared with those reported for antimonic acid and sodium antimonate.

INTRODUCTION

It has been shown earlier¹ that titanium antimonate is a good ion exchanger when such factors as stability in alkaline medium, thermal stability and potential for the separation of inorganic ions are taken into account. It has also been reported that the pH at which titanium antimonate is synthesized is critical for its selectivity for inorganic ions. The selectivity for metal ions and the extent of crystallization of the inorganic ion exchangers have been reported² to be dependent on acid concentration, temperature of the equilibrating solution and the period of ageing of the product with the mother liquor. However, the effects of dilution of parent reagents and their volume ratio of mixing on the selectivity, composition, stability and extent of crystallization of the exchanger have not been determined. It was therefore decided to study these factors with respect to the synthesis of titanium antimonate extensively.

EXPERIMENTAL

Reagents

15% (w/v) titanium (IV) chloride (B.D.H.) and antimony pentachloride (density 2.3 g/ml) (B.D.H) solutions were diluted with 4*M* hydrochloric acid to prepare solutions of required strength. All other reagents were of AnalaR grade.

Apparatus

An Elico pH-meter model LI-10, a Bausch and Lomb Spectronic-20 colorimeter, a temperature-controlled "Sico" shaker, and a Philips camera with a Philips X-ray unit, were used for pH measurements, spectrophotometry, shaking and X-ray studies, respectively. A Perkin-Elmer Model 137 spectrophotometer was used for IR studies.

Synthesis

Solutions of different concentrations of titanium (IV) chloride and antimony pentachloride were mixed in the volume ratios as given in Table I. Ammonia solution was then added dropwise with constant shaking until the pH was zero. All other details for the synthesis of titanium antimonate were similar to those given in our earlier paper¹.

The composition, pH titrations, chemical stability and ion-exchange capacity were determined as reported earlier¹. For X-ray studies, nickel-filtered Cu-K_α radiation was used. The KBr disc method was used for IR studies.

K_d values

The *K_d* values for metal ions were calculated by using the following expression:

$$K_d = \frac{V - I}{I} \times \frac{50}{0.50}$$

where *V* is the volume of EDTA consumed by the original solution and *I* is the volume of EDTA consumed after equilibrium. The total volume of the solution is 50 ml and the amount of exchanger used is 0.50 g. Uranyl ions were determined spectrophotometrically using hydrogen peroxide². All other cations were estimated by titration with 0.002*M* EDTA. The preparation of the column for separation studies and its characteristics were similar to those reported earlier¹.

RESULTS

Physical properties

Samples A, B and F were found to be unstable in water and dilute solutions of mineral acids and were not suitable for column operation, while samples C, D, E and G were quite stable in water, organic solvents and acid solutions. Some of the properties are summarized in Table I.

Chemical properties

The chemical compositions, ion-exchange capacities and chemical stabilities are recorded in Table I. The pH titration curves for samples A, B, C, D, E and G seem to show that the exchanger is monofunctional (Fig. 1) or that the hydroxyl ions are taken up in a hydrolysis process.

X-ray studies

X-ray powder diffraction patterns are shown in Fig. 2. The *d* values for samples C, D and F were found to be similar to those of titanic oxide (rutile, ASTM card

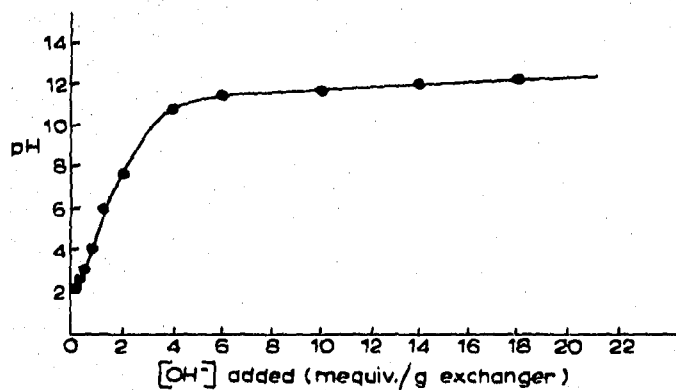


Fig. 1. pH titration curve for titanium antimonate.

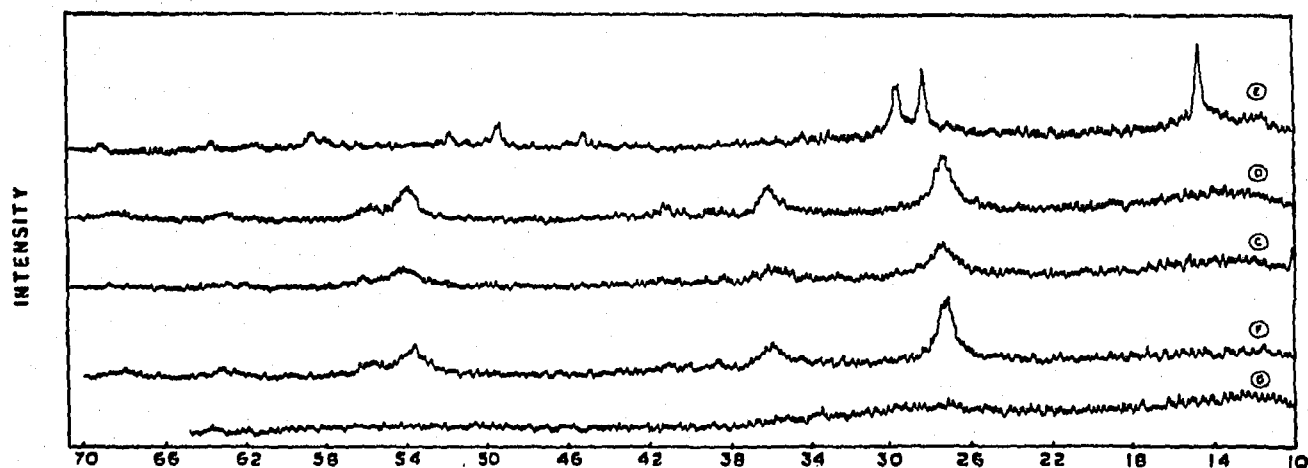


Fig. 2. X-ray diffraction patterns of titanium antimonates.

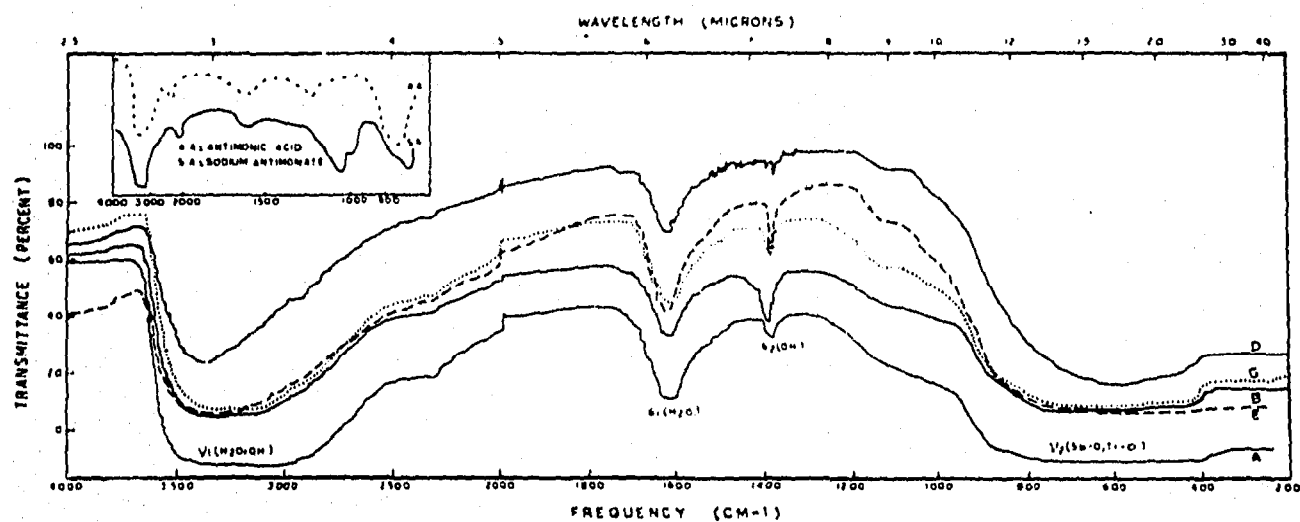


Fig. 3. Infrared spectra of five chemically different titanium antimonates, antimonic acid and sodium antimonate.

No. 4-0551). The d values for semicrystalline sample E are compared with literature values for antimoninic acids and antimony pentoxide in Table II.

TABLE II

COMPARISON OF THE d VALUES OF TITANIUM ANTIMONATE, ANTIMONIC ACID AND ANTIMONY PENTOXIDE

Titanium antimonate ^a		Antimoninic acid ^b		Antimony pentoxide ^c		Antimoninic acid ^d	
$d(\text{\AA})$	I/I_0	$d(\text{\AA})$	I/I_0	$d(\text{\AA})$	I/I_0	$d(\text{\AA})$	I/I_0
6.021	100	5.985	100	6.000	100	5.831	100
3.140	80	3.128	80	3.100	80	3.097	62-70
3.015	65	2.995	75	2.970	80	2.957	62-70
2.004	25	2.594	15	1.820	50	2.500	14-17
		1.998	17				
1.847	35	1.835	31	1.550	30	1.981	14-18
1.757	25	1.754	22	1.150	4	1.822	31-36
1.509	25	1.505	24	—	—	1.741	22-23
						1.555	22-29

^a Present work with Cu.

^b ITO AND ABE² with Cu.

^c HANAWALT AND RINN⁴ with Mo.

^d BAETSLE AND HUYS⁶.

IR studies

The IR spectra are shown in Fig. 3 and indicate the occurrence of stretching and deformation vibrations. The IR spectra of antimoninic acid and sodium antimonate are also given in Fig. 3 for comparison.

Sorption studies. Separation of VO^{2+} from various metal ions

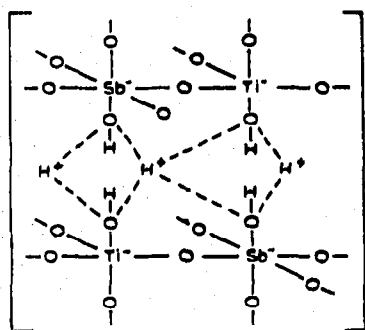
The Kd value of VO^{2+} is very small compared with those of other metal ions. Vanadyl ions were therefore eluted with water. Other metal ions retained in the column were eluted by eluants as listed later in Table IV.

DISCUSSION

Our results show that in addition to the acid concentration, temperature and ageing period, the concentration of the parent reagents and their mixing ratios are also important factors in the synthesis of inorganic ion-exchange materials. Thus sample E, prepared by mixing 0.2M solutions of titanium(IV) chloride and antimony pentachloride in a volume ratio of 1:1, is the most stable sample. Its atomic arrangement is more regular than those of other samples because of its crystalline behaviour. The higher value of the ion-exchange capacity of sample E (Table I) compared with those of the other samples confirm this fact. The ion-exchange capacity of sample E is, however, less than that of antimoninic acid, possibly owing to the absence of free antimoninic acid in titanium antimonate.

The X-ray studies show that samples C, D and F have two phases: (I) titanite oxide and (II) titanium antimonate; coprecipitation of titanium hydroxide with titanium antimonate may therefore have occurred. Sample G is amorphous and

shows gel character as it was prepared in dilute solutions. The d values for the semicrystalline sample E are similar to those reported for antimononic acid and antimony pentoxide². The IR spectra of titanium antimonate show four peaks. A broad but strong peak at about 3250 cm^{-1} is the characteristic stretching vibration of coordinated water molecules. A sharp peak at 1600 cm^{-1} corresponds to the deformation vibration of free water molecules, while the sharp peak at 1400 cm^{-1} is due to the deformation vibration of hydroxyl groups. A broad and weak peak at $400\text{--}800\text{ cm}^{-1}$ may correspond to both the Ti—O stretching (500 cm^{-1}) and Sb—O stretching (625 cm^{-1}). The overlapping of these two similar frequencies may be responsible for the broadness of the peak at lower frequency, while the broadening of the peak at higher frequency may be due to the strongly coordinated water molecules. It may therefore be said that the constitution of titanium antimonate (sample E) is similar to that of antimononic acid with the additional incorporation of titanium atoms. On the basis of chemical composition and these observations, the most probable structure of the semicrystalline titanium antimonate (sample E), $\text{H}_2\text{TiO}_3 \cdot \text{Sb}_2\text{O}_3 \cdot (\text{OH})_3$, can be given as follows:



The solubility data show that the semicrystalline sample is more stable than the poorly crystalline and amorphous products. This observation is in accordance with that reported by ITO AND ABE².

The magnitude of the Kd values for titanium antimonate in aqueous medium is very high compared with those for the molybdate⁶, tungstate⁷ and arsenate⁸ of titanium. Table III shows that in water the Kd values on titanium antimonates are too high to differentiate in the comparative selectivity for metal ions. In order to illustrate the selectivity of titanium antimonate for metal ions, the Kd values were determined at pH 2 (Table III). The selectivity sequence for the most common inorganic ions on organic resins has been reported⁹ to be $\text{Ba}^{2+} > \text{Pb}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Mg}^{2+} > \text{UO}_2^{2+}$.

However, the selectivity sequence on titanium antimonate at pH 2 varies from sample to sample, but there is no complete reversal in the order of the Kd values as reported in our earlier paper¹. The selectivity sequence of metal ions on different samples of titanium antimonate is found to be as follows: sample C = $\text{Pb}^{2+} > \text{Ba}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Cd}^{2+} > \text{Sr}^{2+} > \text{UO}_2^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$; sample D: $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Na}^{2+} > \text{Zn}^{2+} > \text{UO}_2^{2+} > \text{Co}^{2+} > \text{Cd}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Ni}^{2+} > \text{Mg}^{2+}$; sample E: $\text{Cd}^{2+} > \text{Ba}^{2+} > \text{Pb}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Cu}^{2+} > \text{UO}_2^{2+} > \text{Zn}^{2+} > \text{Mg}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+}$; sample G: $\text{Ba}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+} > \text{Sr}^{2+} > \text{Co}^{2+} > \text{UO}_2^{2+} > \text{Ca}^{2+} > \text{Ni}^{2+} > \text{Mg}^{2+}$.

TABLE III
 DISTRIBUTION COEFFICIENTS OF METAL IONS ON TITANIUM ANTIMONATE

Metal ion	<i>Kd</i> values at pH 6-7				<i>Kd</i> values at pH 2			
	Sample C	Sample D	Sample E	Sample G	Sample C	Sample D	Sample E	Sample G
Zn ²⁺	720.00	1540.00	446.66	1540.00	446.00	105.00	49.99	1540.00
Cd ²⁺	680.00	1118.74	2500.00	1060.00	100.00	51.11	1461.00	420.00
Hg ²⁺	0.00	161.12	273.33	77.55	9.23	1.42	255.00	1.42
Mg ²⁺	82.22	58.18	82.22	446.00	9.33	2.50	25.00	22.65
Ca ²⁺	244.00	244.00	473.33	1620.00	32.30	22.85	186.00	91.11
Sr ²⁺	580.00	2166.66	955.53	1260.00	120.66	40.10	353.32	240.00
Ba ²⁺	1360.00	7200.00	1725.00	7200.00	1360.0	108.61	1360.00	3550.00
Pb ²⁺	8000.00	8000.00	8000.00	8000.00	1500.00	700.0	700.0	300.00
Mn ²⁺	440.00	523.01	305.00	710.00	1025.0	8.00	24.60	1025.00
Fe ³⁺	470.00	680.00	220.00	2300.00	860.0	5700.0	353.32	860.00
Co ²⁺	300.00	700.00	1500.00	1500.00	425.00	77.77	14.30	166.66
Ni ²⁺	228.00	1520.00	305.00	710.00	1025.00	21.33	8.00	80.00
Cu ²⁺	740.00	2700.00	1380.00	3260.00	730.00	453.33	137.11	730.00
Al ³⁺	3200.00	3200.00	330.00	3200.00	0.00	0.00	32.00	120.00
Ga ³⁺	3000.00	3000.00	210.00	540.00	520.00	210.00	55.00	210.00
In ³⁺	9000.0	810.00	102.00	9000.00	1720.00	506.66	355.00	736.36
Se ³⁺	---	---	---	---	86.66	86.66	450.00	4500.00
VO ²⁺	---	---	---	---	350.00	350.00	60.00	60.00
Y ³⁺	---	---	---	---	320.00	40.00	320.00	2000.00
Zr ⁴⁺	---	---	---	---	540.00	6200.0	6200.00	6200.00
La ³⁺	---	---	---	---	2200.00	140.00	1400.00	2200.00
Ce ³⁺	---	---	---	---	5400.00	180.00	450.00	2700.00
Pr ³⁺	---	---	---	---	1115.55	68.18	226.66	1860.00
Nd ³⁺	---	---	---	---	1760.00	80.00	272.00	1760.00
Sm ³⁺	---	---	---	---	940.00	108.00	420.00	T.A. ^a
Hf ⁴⁺	---	---	---	---	3500.00	7000.00	7000.00	7000.00
UO ₂ ²⁺	---	---	---	---	85.00	85.00	85.00	131.12
Th ⁴⁺	---	---	---	---	5800.00	5800.00	5800.00	5800.00

^a T.A. = total adsorption.
 TABLE IV
 SOME SEPARATIONS ON TITANIUM ANTIMONATE (SAMPLE E) COLUMNS

Separation	Eluants	Volume of effluent (ml)	Amount of cation loaded (μg)	Amount of cation recovered (μg)	Amount of exchanger taken (g)
VO ²⁺ - Fe ³⁺	VO ²⁺ - H ₂ O	15	680	680.00	1.50
	Fe ³⁺ - 1M NH ₄ Cl + 0.1 M HCl	15	1211.7	1211.7	
VO ²⁺ - Al ³⁺	VO ²⁺ - H ₂ O	15	680	680	1.00
	Al ³⁺ - 1M NH ₄ Cl + 0.1 M HCl	15	1160.00	1160.00	
VO ²⁺ - Mn ²⁺	VO ²⁺ - H ₂ O	15	680	680	1.00
	Mn ²⁺ - 5% NH ₄ Cl	30	1484	1484	
VO ²⁺ - UO ₂ ²⁺	VO ²⁺ - H ₂ O	15	680	680	1.00
	UO ₂ ²⁺ - 0.1M HCl + 1M NH ₄ Cl	30	3500	3500	
VO ²⁺ - Zr ⁴⁺	VO ²⁺ - H ₂ O	15	680	680	1.00
	Zr ⁴⁺ is very difficult to elute	---	1208	1208	
VO ²⁺ - Hf ⁴⁺	VO ²⁺ - H ₂ O	15	680	680	1.00
	Hf ⁴⁺ is very difficult to elute	---	---	---	

These sequences show that there is no complete reversal in the order of the Kd values; this deviation may be due to the varying composition and conditions of preparation of the samples. The pH at which the synthesis is done is therefore more important than the variation in composition with regard to the reversal in Kd values. This conclusion is supported by the work of VESELY AND PEKAREK¹⁰ on zirconium phosphate. The analytical utility of the semicrystalline titanium antimonate has been illustrated by achieving some important separations of metal ions as shown in Table IV. From the available data, it is not possible to say whether sample E is titanium antimonate or whether it is wholly or partially a mixture of titanium and antimony oxides.

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