

Studies on Polytungstoantimonate Ion Exchanger: Part I—Synthesis, Properties & Ion Exchange Behaviour of Polytungstoantimonate

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A new inorganic ion exchanger, polytungstoantimonate, has been synthesised under different conditions. The composition, chemical stability, physicochemical properties and ion exchange behaviour of polytungstoantimonate are reported and discussed.

During the last two and half decades synthetic inorganic ion exchangers have attracted much attention due to their fair stability towards heat and ionizing radiations and higher selectivity towards certain metal ions in comparison to that of commercial ion exchange resins. Among the different classes of inorganic compounds, insoluble salts of polybasic metal ions and hydrous acidic oxides of metals have been studied greatly and these show important ion exchange properties¹⁻⁴. Although considerable work has been done on these materials, more systematic work still remains to be done on polyacids. The ion exchange behaviour of polyantimonosilicates⁵ has been studied. The present paper reports systematic studies on synthesis, composition, chemical stability, infrared spectra, heat treatment, pH-titration and ion exchange capacity of polytungstoantimonate.

Materials and Methods

pH measurements were made with an ELICO Model LI-10 pH meter (Hyderabad, India). Spectrophoto-

metric measurements were carried out using an ECIL Spectrophotometer Model GS 865B (Hyderabad, India). An OWA Labor type 707-04 analytical balance was used. Perkin Elmer IR spectrophotometer Model 783 was used for IR studies and Shimadzu DT-30 (Japan) was used for TGA and DTA studies.

Antimony pentachloride (Fluka A.G.) was used as such. All the other chemicals and reagents were of A R Grade (BDH/EMerck/S Merck).

Synthesis

Five samples of polytungstoantimonate having different compositions were prepared by mixing 0.1 M solution of antimony pentachloride taken in 4 M HCl/0.05 M aqueous solution of potassium pyroantimonate with 1.2 M/0.6 M sodium tungstate solution in water. The mixture in each case except B1 (Table 1) was acidified with 35 ml of conc. HCl and was digested at steam temperature or refluxed as shown in Table 1. Then the product was allowed to settle; it was filtered and washed with deionised water several times

Table 1—Synthesis and Properties of Polytungstoantimonate

Batch No.	Conc. (mol)		Mixing volume ratio Sb(V): W(VI) _n	Digestion temp. and time (hr)	Colour (state)	W/Sb ratio	H ⁺ ion liberation capacity (meq/g for Na ⁺)
	Sb	W					
B1	0.1(AP)	1.2	1:1	Steam temp. (2)	Yellow (glassy)	15.14	0.81
B2	0.1(PP)	1.2	1:1	Steam temp. (2)	Yellow (glassy)	35.1	0.83
B3	0.1(PP)	0.6	1:1	Steam temp. (2)	Light yellow (glassy)	18.87	0.78
B4	0.1(PP)	1.2	1:1	Refluxed. (8.5)	White (amorphous)	—	0.47
B5	0.1(PP)	1.2	1:1	Steam temp. (8.5)	Light yellow (amorphous)	—	0.61

AP = antimony pentachloride, PP = potassium pyroantimonate

until free from soluble antimony and tungsten. pH of the washing was noted to be 3.1. The product was dried in air, broken down into small particles and sieved into 50-100 mesh size. The material was converted into H⁺ form by shaking with 2 M HNO₃ intermittently for one day, and the excess acid was washed with deionised water. It was first air-dried and then dried *in vacuo* over CaCl₂. The conditions of preparation are summarised in Table 1.

Complete analysis of the exchanger material was done by standard chemical and instrumental methods. Tungsten was determined gravimetrically⁶ as WO₂(C₉H₆ON)₂ and antimony was determined iodimetrically⁶ using standard iodine solution after reduction of Sb(V) to Sb(III) with red phosphorus and iodine. To test the accuracy, tungsten was again determined spectrophotometrically by the standard thiocyanate method⁷ and antimony was estimated spectrophotometrically by the iodide method⁷. Reproducible results were obtained with standard deviation of ± 0.015. The mole ratios W(VI)/Sb(V) are shown in Table 1.

Chemical stability of the samples was tested by weighing accurately about 1 g of the exchanger (50-100 mesh H⁺ form) and shaking with 100 ml of required acid/alkali/salt solution for 4 hr. Tungsten and antimony were determined in the solution spectrophotometrically by the thiocyanate⁷ and iodide⁷ methods respectively.

Results and Discussion

Of the five samples of polytungstoantimonate prepared, exchanger materials B4 and B5 were found to have lower ion exchange capacities in comparison to those of B1, B2, and B3; therefore, further work was carried out with samples B1, B2, and B3 only. Compositions and chemical stabilities of B1, B2 and B3 materials are reported in Tables 1 and 2. From Table 2, it is evident that polytungstoantimonate samples B1, B2 and B3 are stable towards different acids and salts of different strengths. The exchangers have a little leaching tendency with alkali solution, but it is inhibited in presence of salt solution. Column operation with the exchanger can be done at pH 10-11. Due to its higher stability towards acids, the exchanger B1 was selected for further investigation.

The mole ratio of Sb, W and H₂O in polytungstoantimonate (B1) is Sb:W:H₂O = 2:30:12.98. Hence, the probable composition of the material may be written as Sb₂O₅.30WO₃.13H₂O (after drying at 100°C). The probable reactions involved in its formation, based on tetraoxo-acids¹² (coordination number = 4), may be written as,

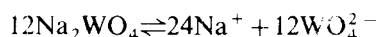
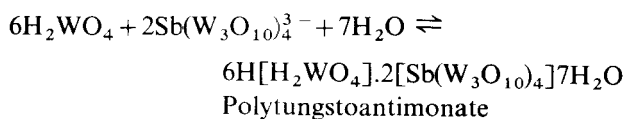
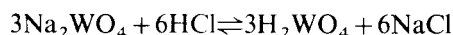
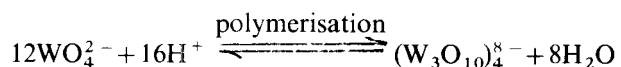


Table 2—Solubility of Polytungstoantimonate in Different Solvents

	Antimony dissolved (mg/100 ml)			Tungsten dissolved (mg/100 ml)		
	B1	B2	B3	B1	B2	B3
DMW	2.75	1.06	1.88	22.5	17.5	25.0
NaCl (2 M)	0.26	0.05	0.31	1.35	2.25	6.55
KCl (2 M)	0.31	0.42	0.71	0.3	1.15	3.00
NH ₄ Cl (2 M)	0.03	0.3	0.37	0.5	1.0	2.1
HCl (1 M)	0.73	1.08	2.03	3.18	5.5	13.0
HNO ₃ (1 M)	0.51	1.16	1.72	3.18	5.5	14.25
H ₂ SO ₄ (0.5 M)	0.95	0.76	1.56	1.25	0.83	2.33
CH ₃ COOH (1 M)	1.31	1.22	2.5	1.5	5.0	17.5
HCl (4 M)	0.76	2.03	3.75	5.5	9.25	15.75
HNO ₃ (4 M)	0.75	1.25	2.34	0.83	1.68	2.93
H ₂ SO ₄ (2 M)	1.16	1.72	3.13	4.25	9.75	14.5



IR spectra

The infrared spectra of polytungstoantimonate (B1) were recorded without heating (a) and after heating (b) at 800°C. A broad absorption band between 3600 and 3200 cm⁻¹ with the maximum at 3400 cm⁻¹ (a)/3450 cm⁻¹ (b) is characteristic of interstitial water molecule and OH groups associated with hydrogen bonding between them and a band between 1700 and 1500 cm⁻¹ with the maximum at 1610 cm⁻¹ (a) is due to the deformation mode of interstitial water molecule. A well defined peak occurring at 350 cm⁻¹ (a) and a broad band between 900 and 600 cm⁻¹ (a) are due to νW-O and νSb-O modes respectively. It indicates also the presence of metal-oxygen polymeric species in the sample. Absorption bands due to OH group decreased in intensity on heating. Shifting of the broad band at 900-600 cm⁻¹ (a) to a sharp peak at 800 cm⁻¹ (b) on heating at 800°C indicates the breaking down of polymeric species and the formation of metal oxide. Absence of sharp peak at 1610 cm⁻¹ (b) indicates the loss of interstitial water molecule on heating.

Heat treatment

About 1 g of the exchanger (B1) was heated at 80°C and from 100°C to 600°C in steps of 100°C in a muffle furnace for one hour; the samples were weighed after

each step of heating. During heating the colour of the sample gradually changed from yellow to light yellow. The difference in weight between 600°C and 100°C was the amount of water lost, and the weight of the residue was the amount of anhydrous antimony (V) oxide plus tungsten (VI) oxide. From this result the water of crystallization was calculated by the method of Alberti *et al.*⁸ H⁺, Na⁺ and K⁺-forms of the exchanger were subjected to thermogravimetric analysis at a heating rate of 10°/min.

It is evident from the analysis that the weight loss for the H⁺ form of the exchanger is greater than that for Na⁺ and K⁺ forms. This is because, removal of structural water after condensation is possible from H⁺ form only. The weight loss of the exchanger is in the order H⁺ form > Na⁺ form > K⁺ form, according to the hydrated radii of these ions.

pH titration

Topp and Pepper's method⁹ was employed for pH titration of the exchanger B1. The pH titrations were performed with different amounts of MOH (M⁺ = Na⁺, K⁺ and NH₄⁺). After shaking for 4 hr at a constant temperature (30 ± 2°C), the pH of the solution was recorded. The experiment was repeated in the presence of salt containing varying amount of MOH and HCl in a ratio such that the total [H⁺] remained constant in every case. Addition of MCl releases more H⁺ from the exchanger and this decreases the pH.

The results show that the exchanger in hydrogen form behaves as a weak dibasic acid in which the first ionization occurs in acidic medium while the second occurs in basic medium above pH 7. Second dissociation step is not complete in the case of aqueous NH₃ due to weak basicity of NH₄OH. The effect is prominent in the case of NH₄Cl + NH₄OH due to formation of buffer system.

Exchange capacity

The effect of concentration of the neutral salt (sodium chloride) and time of equilibration on the exchange capacity of the exchanger were evaluated by batch operation¹⁰.

From the knowledge of optimum eluent concentration (1.5 M) and equilibration time (4 hr), the ion exchange capacity¹¹ for Li⁺, Na⁺, K⁺ and NH₄⁺ ions for different batches was determined at pH 5-6. The results are shown in Table 3. The total ion exchange capacity of the weakly acidic cation exchanger was determined under alkaline condition.

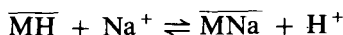
The ion exchange capacity by column elution method was determined by taking about 1 g of the exchanger (B1, H⁺-form, 50-100 mesh size) in a glass column (1.2 cm) and passing 1 M sodium chloride solution (0.86 meq/g). The process was repeated with

Table 3— Ion Exchange Capacity at pH 5-6 for Univalent Cations

Cation	Hydrated ionic radius (Å)	Ion exchange capacity (meq/g)				
		B1	B2	B3	B4	B5
Li ⁺	3.4	0.61	0.57	0.55	0.34	0.45
Na ⁺	2.76	0.81	0.83	0.73	0.47	0.61
K ⁺	2.32	0.93	1.01	0.94	0.54	0.71
NH ₄ ⁺	—	1.01	1.05	0.96	0.70	0.79

0.1 M sodium chloride solution. In each case upto 100 ml of effluent was collected in 5 ml fractions at a flow rate of 0.4-0.5 ml/min and titrated with standard sodium hydroxide solution.

Polytungstoantimonate exhibits cation exchange properties according to the following reaction,



where \overline{MH} represents the hydrogen form of the exchanger. Initially the release of hydrogen ions was fast, as all of the exchange sites were in the hydrogen form and the forward reaction was rapid. Although hydrogen ions were still liberated even after passing 100 ml of sodium chloride solution, their amount was very small and thus neglected. The ability of a cation to displace H⁺ ion is a measure of its selectivity and it is related to the hydrated ionic radius of the cation. As expected, the selectivity order for the monovalent cations in the case of polytungstoantimonate is: NH₄⁺ > K⁺ > Na⁺ > Li⁺.

A plot of hydrated radii of monovalent alkali metal cations against ion exchange capacity gave a straight line (Fig. 1). The total ion exchange capacities for Na⁺, K⁺, and NH₄⁺ ions were found to be 2.4, 3.9, and 2.4 meq/g respectively. The ion exchange capacities of the exchanger B1 after drying at 80°C, 100°C, 200°C and 300°C were 0.59, 0.45, 0.33 and 0.25 meq/g

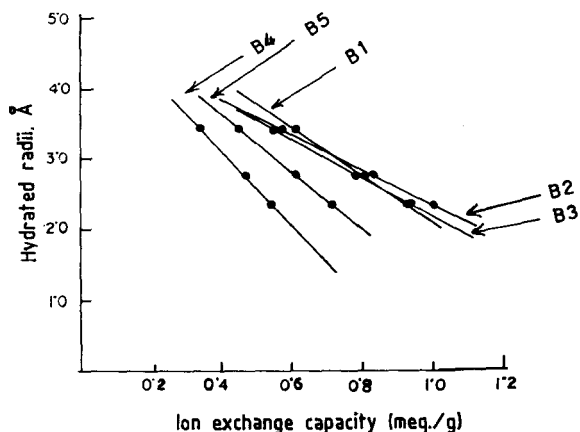


Fig. 1— Ion exchange capacity as a function of hydrated radii of alkali metal ions

respectively. It reveals that the ion exchange capacity of the exchanger decreases with increase in temperature.

Regenerative ion exchange capacity of the exchanger B1 was also determined for three cycles using 2 M HNO₃ as the regenerant. The ion exchange capacity for Na⁺ after each cycle was noted to be 0.69, 0.68, and 0.65 meq/g respectively. It is evident from the above results that the exchanger has good regenerative capacity. From the compositions of the exchanger B1 it is noted that the exchanger material is made of large quantities of WO₃ and H₂O molecules containing a little amount of Sb₂O₅. Hence the exchange capacity of the exchanger should be mainly due to WO₃ · x H₂O. It is interesting to note that ion exchange capacity of hydrous WO₃ (0.048 meq/g for Na⁺) as reported by De and Chowdhury¹³ is much less than the ion exchange capacity of the material under investigation. If the material were a mixed oxide, it should have low ion exchange capacity like that of hydrous WO₃. Ion exchange capacity of the material B1 (0.81 meq/g for Na⁺) clearly indicates that it is not a mixed oxide, and probably it is a heteropoly acid salt.

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