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Hydrous Tantalum Phosphates for Ion Exchange Purposes. A Systematic Study

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This work describes two methods of preparation of hydrous tantalum phosphates and their characterization as ion exchangers. The hydrous metallic phosphate compounds were chemically and physically characterized by thermal gravimetric analysis, X-ray diffractometry and surface area measurements. By the first method, tantalum phosphate was prepared by alkaline fusion of Ta_2O_5 with an excess of K_2CO_3, followed by lixiviation of the tantalate fusion product with hot water, and precipitation with diluted H_3PO_4. Preparation II was performed using metallic Ta dissolved in concentrated HF/HNO_3 acidic mixture followed by hydrolysis of fluortantalic acid intermediary and precipitation with diluted H_3PO_4. Both freshly prepared materials (I and II) were exaustively refluxed with concentrated H_3PO_4, in its boiling point temperature, resulting respectively in Ta_2O_5. 2.1 H_2O, (IR) and Ta_2O_5. 1.3 H_2O, (IIR). Characterization of the prepared products have presented the following values: surface area of 108.27 ± 2.80; 220.14 ± 2.67; 117.07 ± 5.25 and 141.61 ± 0.27 $m^2.g^{-1}$ respectively for I, IR, II and IIR. All these materials were amorphous. The ion exchange behavior for all four hydrous tantalum phosphates was studied using Na^+, K^+ and Ba^{+2} as the exchanged species. The values for typical ion exchange capacity were 1.64; 1.23; 1.47 and 1.01 miliequivalent.g^{-1}, respectively for I, IR, II and IIR products.

Keywords: *hydrous tantalum phosphate, ion exchange, cationic exchanger*

1. Introduction

Over the past few decades, ion exchange behavior was thought to be confined to a very limited number of inorganic compound types. However, as works progressed in this area, it has come to be recognized that ion exchange properties were presented by many different classes of compounds in literature[1,2].

The importance of synthetic inorganic ion exchangers has increased selectivity, stability at elevated temperatures and resistence to high radiation fields. Among the inorganic ion exchange materials described, hydrous antimony oxides, titanium, tin(IV) and manganese compounds have been studied extensively[1].

Hahn[3] observed that niobium and tantalum forms stable phosphate salts, as amorphous and hydrated precipitates, when their corresponding potassium niobate or tantalate solutions were treated with an excess of phosphoric and nitric acids. The precipitates obtained lose water and became crystalline upon ignition. Data were presented to show that $NbOPO_4$ and $TaOPO_4$ were the most likely formulas for the ignited compounds. Later, it was shown that tantalum phosphates might be obtained from phosphoric acid solutions containing hydrofluoric acid starting from tantalum pentoxide[4,5]. The sorption properties of the tantalum phosphate prepared from solutions containing fluoride studied by Rakhmatulin and coworks[6].

The ion exchange properties of tantalum phosphates were studied for cesium ions[4] in a batch process. Their ion exchange capacity is mantained up to 250 °C but decreases consideravely with the increase of the temperature because the phosphate dehydrates and their sorption capacity breaks down[4].

Hölgie and coworks[4,5] studied the use of the tantalum phosphate for the separation of ^{95}Zr-^{95}Nb from other fission products both by coprecipitation with the precipitate and by sorption on tantalum phosphate previously prepared.

Tantalum phosphate dihydrate of high crystallinity has been prepared by Yaroslavtsev and Nikolaev[7]. $KTa(PO_4)_2$ was obtained from reaction of Ta_2O_5 and KH_2PO_4 at

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1000 °C, giving , as products, meta and pyrophosphates. The mixture was treated with diluted HCl and H_3PO_4 to produce $HTa(PO_4)_2.2H_2O$. The ion exchange behavior of this acidic phosphate was studied for Li^+, Na^+ and K^+ ions[8] and their thermodynamic parameters were evaluated.

Tarnopolskii and coworks[9] studied the processes accompanying thermal treatment in the HTa $(PO_4).2\ H_2O + MCl_x$ (for $M^{+x} = Na^+, K^+, Rb^+, Cs^+$) systems. It was found that mechanochemical ion exchange interation proceeds in these mixtures in the course of grinding. Introducing alkali metal cations into the phosphate crystal lattice during the mechanochemical treatment increases the dehydration tempertaure of the acid tantalum phosphate and decreases the onset temperature of ion exchange. The diffusivities of cations in the products of exchange were evaluated at 430, 460 and 490 °C. The calculated diffusivity for the specified temperature range trends to increase with increasing radius of the alkali metal cation.

Tarnopol'skii and cowoorks[10] have also studied the exchange of protons by alkali metal ions on acid tantalum phosphate, $H_5O_2Ta(PO_4)_2$ and the interdiffusion coefficients in the resulting solid solutions were evaluated. The mobility of alkali metal cations was found to decrease in the order $D_{K+} > D_{Li+} \sim D_{Na+} >> D_{Cs+}$.

In this work, some synthetic routes for preparation of hydrous tantalum phosphates ($TaOPO_4.\ n\ H_2O$) are described. Their characterization and ion exchange behavior were also studied.

2. Experimental

2.1. Materials and methods

Ta_2O_5 was prepared by purification of the brazilian tantalite ore using liquid-liquid solvent extraction in hydrofluoridric sulphuric acid media in our Institution.

Pure metallic tantalum was produced in our Institution at a pilot plant in the Materials Department by aluminothermic reduction of Ta_2O_5 with an excess of metallic Al followed by refine in an electron beam furnace.

All aqueous titration solutions were prepared with deionized water and were previously standardized before use.

2.2. Preparation of the hydrous tantalum phosphates

2.2.1. Preparation I

Ta_2O_5 was mixed with a ten fold excess of K_2CO_3. The mixture was homogeneized and ignited at 1000 °C for 12 h. The resulting melt material was lixiviated and dissolved with hot H_2O, filtered and the hydrous metallic phosphate precipited by addition of 3.0 mol.L^{-1} H_3PO_4 acidic solution at a 1:2 Ta/phosphate ratio. The precipitate obtained was washed with deionized water until pH 5 and dried at room temperature in a dissecator.

2.2.2. Preparation II

Metallic Ta was dissolved in HF/HNO_3 concentrated acids in a 1:3 ratio. Then enough quantity of a 0.3 mol.L^{-1} H_3PO_4 acidic solution to achieve a 1:2 Ta/phosphate ratio was slowly added; then sulphuric acid sufficient to obtain a final 3.0 mol.L^{-1} H_2SO_4 concentration was also added. The resulting solution was heated for 120 h at 60 °C for slow precipitation of the hydrous tantalum phosphate. The resulting precipitate was filtered, washed with deionized water until pH 5, and dried at room temperature in a dissecator.

2.2.3. Preparations IR and IIR

The compounds IR and IIR were prepared by refluxing newly formed hydrous tantalum phosphates I and II, whose preparations were described above based in the literature procedure for similar materials[9,10]. Both materials were treated with concentred H_3PO_4 (12 mol.L^{-1}) in this boiling point for more than 300 h. The gelatinous solids obtained were filtered, exaustively washed with deionized water until pH 5 and dried at room temperature in a dissecator.

2.3. Characterization of hydrous tantalum phosphates

All hydrous tantalum phosphates were characterized by thermal analysis and their crystallinity studied by powder diffractometry. The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were obtained with a Shimadzu Thermoanalyser, model TGA-50 at a heating rate of 10 °C.min^{-1} in an atmosphere of nitrogen, between 30 and 800 °C. X-ray diffraction measurements were obtained with a Rich Seifert equipment, model ISO-Debyflex 100 using CuKα radiation, for 2θ values between 5 and 80°. Their surface areas, S_{BET} in $m^2.g^{-1}$ were determined by nitrogen adsorption from BET methodology, in a Micrometrics equipment, Flow sorb 2300 model, beforehand the samples were degassed in the cell at 50 °C for 3 h.

2.4. Ion exchange behaviour

2.4.1. Reversibility of the exchanger process

A sample having 0.0500 g sample of the hydrous tantalum phosphate was mixed with 50.00 mL of MCl 0.1000 eq.L^{-1} solution, and titred with a [MCl 0.05000 + MOH 0.05000] eq.L^{-1}, for $M^{+n} = Na^+, K^{+1}$ aqueous solution until pH 11.0. The reverse reaction, the regeneration of the ion exchanger material, was performed in the same way, by titration the resulting solution with a [HCl 0.1000 + MCl 0.10000] eq.L^{-1}, for $M^{+n} = Na^+, K^+$, aqueous solution until the pH reaches to the initial value. The exchange and regeneration steps were repeated to investigate the reversibility of the exchange process.

Similar titration procedures were performed with Ba^{+2} ions using respectively 50.00 mL of $BaCl_2$ 0.2000 eq.L^{-1} and as the titrating [$BaCl_2$ 0.1000 + $Ba(OH)_2$ 0.1000] eq.L^{-1} aqueous solution for the direct procedures and [HCl 0.1000 + $BaCl_2$ 0.2000] eq.L^{-1} for the titrations in the regeneration steps.

2.4.2. Exchange capacity measurements

A second procedure was used to study the exchange process.It was performed in a batch way using 0.0500 g samples and different OH^- equivalent quantities. The pH was risen by mixing volumes with increments of the [MCl 0.05000 + MOH 0.05000]eq.L^{-1}, for $M^{+n} = Na^+, K^+$ aqueous solution and enough volumes of MCl 0.1000 eq.L^{-1}, for $M^{+n} = Na^+, K^+$, to complete 50.00 mL, in order to mantain the same total metallic ion concentration for all samples. The solutions with the exchanger were stirred and the pH measured for different exchange times.The exchange capacities were determined by the inflexion of the experimental curves pH versus OH^- miliequivalent obtained, whose corresponds to the exchanged M^{+n} species exchanged between the exchanger and the solutions.

3. Results and Discussion

Amorphous materials (preparations IR and IIR) were obtained by reflux newly formed amorphous hydrous tantalum phosphates in discordance with the results obtained by Suarez *et al.* described in literature[11,12].

All the compounds of $TaOPO_4.nH_2O$ were characterized by thermal analysis, (TG) and the results obtained are listed in Table 1. The weight loss, from 30 to 400 °C was attributed to dehydration of the interstitial water molecules. However, the TG curves showed a continuous weight loss between 400 and 800 °C that was associated to the transformation of hydrogenphosphate into pyrophosphate[11,12] groups.

Typical TG curve obtained for the product IR was shown in Fig. 1. The TG curves for all prepared materials show similar behavior.

The chemical composition of the prepared phosphates was stablished from the thermogravimetric curves, which can indicate the amount of water held in the solid (first step on Table 1 for each material, in temperature range 30-400 °C), by expression:

$$18\ n = X\ (M + 18\ n)\ /\ 100$$

where X is the weight loss percentual;
n the number of external water and;
M is the molecular weight without water molecules.

Table 2 shows the chemical composition obtained from the thermogravimetric results. It can be observed that the products IR and IIR presented a smaller number of hydration waters than the products without refluxing I and II. Amorphous forms of the all hydrous tantalum phosphates were obtained by X-ray diffraction analysis.

Suárez and coworks[11] showed, however, that crystalline hafnium phosphate was prepared by refluxing newly formed amorphous hafnium phosphate in concentrated H_3PO_4, in their boiling point, for more than 210 h. For our

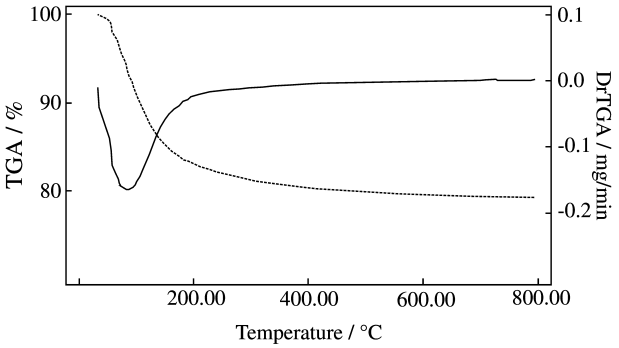


Figure 1. Thermal gravimetric analysis results of hydrous tantalum phosphate (preparation IR).

Table 1. Chemical composition of hydrous tantalum phosphates, obtained by thermal gravimetric analysis and surface area determined by BET methodology.

Preparation	Temperature range (°C)	Weight loss (%)	Chemical composition	Surface area ($m^2.g^{-1}$)
I	30-400	17.2	$TaOPO_4.3.4\ H_2O$	108.27 ± 2.80
	400-800	1.4		
IR	30-400	11.3	$TaOPO_4.2.1\ H_2O$	220.14 ± 2.67
	400-800	1.1		
II	30-400	12.5	$TaOPO_4.2.3\ H_2O$	117.07 ± 5.25
	400-800	1.1		
IIR	30-400	7.3	$TaOPO_4.1.3\ H_2O$	141.61 ± 0.27
	400-800	2.1		

refluxed materials this phenomenon was not observed like shown the X-ray diffractograms of Fig. 2.

It is difficult to explain why we didn't obtain some crystalinity in our compounds however literature describes the obtaintion of crystalline tantalum phosphate when the preparation takes place at high temperature and pressure values[6,13] .This conditions were quite different of those employed in our experiments. The possibility of thermal treatment of the solid tantalum phosphates was to discard because the water molecules were displaced at low temperatures in all prepared compounds.

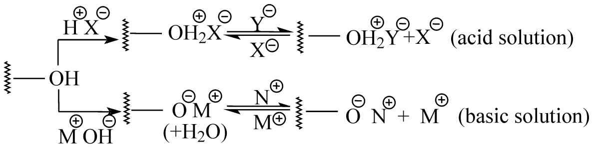
Surface area measurements, were determined by BET methodology and the results obtained described in Table 1. The values obtained shows that the refluxed materials presented greater surface areas than the original ones.

Ion exchange behavior was studied by two differents procedures, using titrimetric detection with the aid of a glass combined electrode measuring the pH of aqueous solutions of the exchanged cations studied in contact with the hydrous tantalum phosphates.

Beside the ion exchange experiments were an indirect way to study the ion exchange process it is an usual way to study the ion behavior and may be sumarysed by Scheme 1.

In the first procedure we may study the reversibility of the exchange by repetition of the exchange and regeneration steps in an indirect manner by titration of the H^+ ions exchanged by each of the metallic exchanged species, M^{+n}, for $M^{+n} = Na^+$, K^+ and Ba^{+2}.

The second procedure, realized in a batch way, permits to determine the ion exchange capacity for each ion M^{+n} studied , for $M^{+n} = Na^+$, K^+ and Ba^{+2} at different agitation times. This procedure is similar to the rapid titration method used to study the reversibility of the inorganic exchanger but permits to construct the pH x OH^- miliequivalent curves at different stirring times for obtention of equilibrium exchange capacities. Figures 3 and 4 show typical results obtained for Na^+ exchange studies.



Scheme 1.

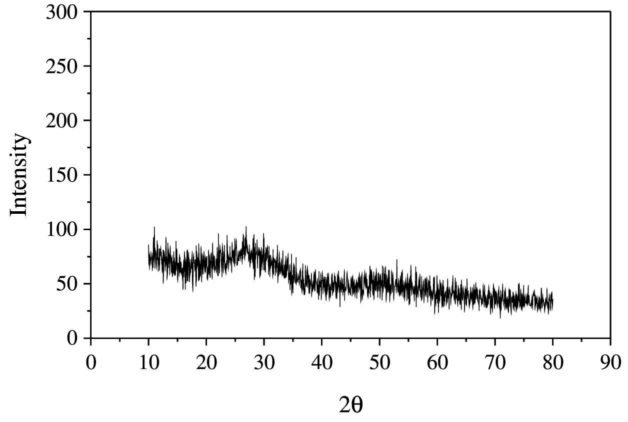


Figure 2. X-ray diffractogram obtained for hydrous tantalum phosphates.

Figure 3 shows that the hydrous tantalum phophate exchanger material is partially regenerable before three consecutive exchage steps.

Plots of pH as a function of stirring time or of pH x OH^- were used to determinations of the exchange capacities for each prepared material. Figure 4 showed the behavior for Na^+ exchange with preparation I. The results show that for times longer than four hours the ion exchange capacities are maximum.

Table 2 shows the results of ion exchange capacities, (IEC) obtained with Na^+, K^+ and Ba^{+2} ions (batch process). It can be observed that the compounds I and II present better IEC values than the refluxed compounds IR and IIR. This is in agreement with the results obtained for the number of external water molecules (see Table 1) that shows that compounds I and II have higher hydration numbers. Analy-

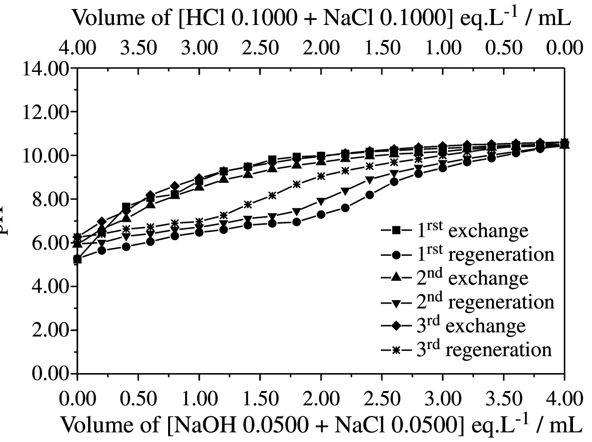


Figure 3. Reversibility study of ion exchange and regeneration process for Na+ ions using 0.0500 g of hydrous tantalum phosphate (preparation IR).

Table 2. Results of ion exchange capacities (IEC) with Na^+, K^+ and Ba^{+2} ions.

Preparation		IEC	
	Na^+	K^+	Ba^{+2}
		(OH^- milieq.g^{-1})	
I	1.64	1.54	5.54
IR	1.23	1.32	4.67
II	1.47	1.59	7.82
IIR	0.61	0.56	5.46

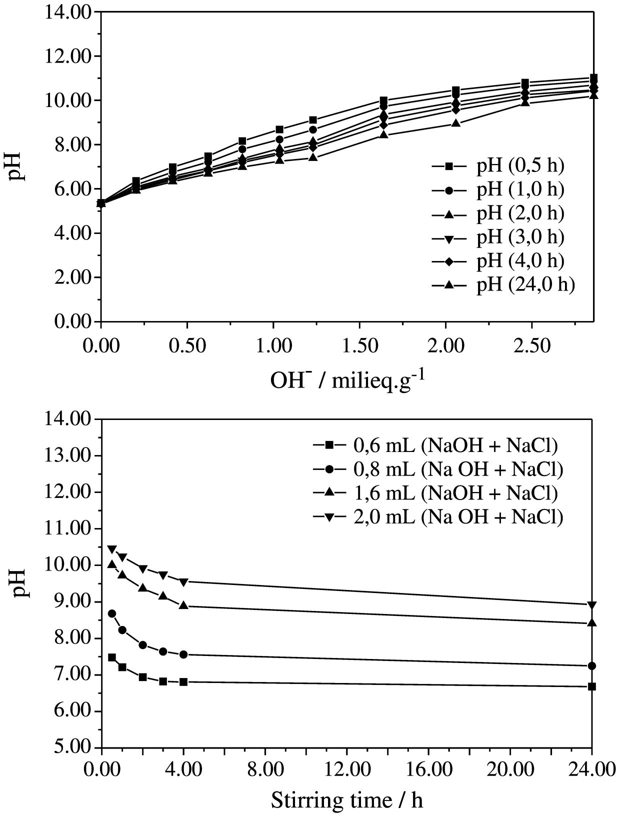


Figure 4. Typical ion exchange curves obtained for Na+ ions exchange with hydrous tantalum phosphate (preparation I).

sis of the adsorption data shows that in basic solution materials I and IIR preferably adsorbs sodium ions (1.64 and 0.61 meq.g^{-1} respectively). The materials IR and II preferably adsorbs potassium ions (1.23 and 1.47 meq.g^{-1} respectively). By the way, the surface areas for compounds I and II are smaller than for the refluxed materials IR and IIR (see Table 1).

4. Conclusion

The hydrous tantalum phosphates I, IR, II and IIR obtained did not present crystalline structures after or before refluxing with concentrated H_3PO_4. Its amorphous forms show relatively high surface areas. Their physico-chemical properties, and their ion exchanger capacities in aqueous solutions of alkaline/alkaline earth elements (Na^+, K^+ and Ba^{+2}) show that those materials can be considered as promising ion exchanger materials.

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