Ion-exchange in acid tantalum phosphate

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The cation-exchange process (H^+/M^+, $M^+ = Li^+, Na^+, K^+$) for acid tantalum phosphate in solutions has been studied and an evaluation of the thermodynamic parameters for this process made.

It is common knowledge that some polyvalent element phosphates exhibit pronounced ion-exchange properties.[1,2] Unlike materials based on an organic matrix a regular arrangement of functional groups often provides high selectivity of these compounds for cations of various sizes. Such typical representatives of this class as acid zirconium, tin and titanium phosphates have been intensively studied for the last few decades.[3–5] The similarity of the basic structural features and the high mobility of proton-containing groups allows us to expect similar properties for acid antimony and tantalum phosphates recently studied by us.[6,7] Chernorukov *et al.* established[8] that a study of the ion-exchange properties of acid tantalum phosphates in solutions is impossible because of its low resistance towards hydrolysis which depended strongly on the degree of crystallinity of the compound. Use of macrocrystalline acid tantalum phosphate proved to be more promising.[7]

Macrocrystalline acid tantalum phosphate was prepared according to the method described in ref. 7. pH-Titration of acid tantalum phosphate by 0.1 mol dm^{-3} LiOH, NaOH and KOH in the presence of a triple excess of the appropriate 0.1 mol dm^{-3} chloride at temperatures 292, 313 and 300 K was carried out using a pH-millivoltmeter pH-121. During the titration process the following equilibrium (1) occurs:

$$xM^+ + HTa(PO_4)_2 \longleftrightarrow xH^+ + M_xH_{1\text{-}x}Ta(PO_4)_2 \qquad (1)$$

Addition of alkali leads to neutralization of the protons in solution. Moving to the equilibrium leads to a further release of protons from the matrix. To avoid hydrolysis the titration was carried out in the range $pH < 7$. This allows us to avoid completely the possible hydrolysis of macrocrystalline acid tantalum phosphate. At the equivalence point ($pH \approx 7$), which corresponds to a maximum rate of pH increase (dpH/dV), the proportion of exchanged protons is 1.00 ± 0.02. This is supplementary evidence for the purity of the acid tantalum phosphate obtained.

In the case of titration of acid zirconium phosphate, which has a structure similar to acid tantalum phosphate, Alberti[9] established the coexistence of two solid phases: either $H_2Zr(PO_4)_2 \cdot nH_2O$ and $MHZr(PO_4)_2 \cdot nH_2O$, or $MHZr(PO_4)_2 \cdot nH_2O$ and $M_2Zr(PO_4)_2 \cdot nH_2O$. Thus, in the titration of fully crystalline $HTa(PO_4)_2 \cdot 2H_2O$ this model provides constancy of pH if the concentration of M^+ is nearly invariant, reaction (2):

$$HTa(PO_4)_2 \cdot 2H_2O + M^+ + (n\text{-}1)\,H_2O \longleftrightarrow MTa(PO_4)_2 \cdot nH_2O + H_3O^+ \qquad (2)$$

However, the titration curve for $HTa(PO_4)_2 \cdot 2H_2O$ is characterized by a continuous increase in pH. This allows us to propose the formation of solid solutions of composition $M_xH_{1-x}Ta(PO_4)_2 \cdot nH_2O$.

To confirm this proposal the titration of acid tantalum phosphate in 0.1 mol dm^{-3} KCl by potassium hydroxide was interrupted at a *design point* of 50% substitution. The solid phase was filtered off and dried out. The results of an X-ray diffraction study showed that the substance obtained was monophasic and the interlayer spacing lies between that of $HTa(PO_4)_2 \cdot 2H_2O$ and $KTa(PO_4)_2 \cdot nH_2O$. This confirms the formation of a solid solution $K_xH_{1-x}Ta(PO_4)_2 \cdot nH_2O$.

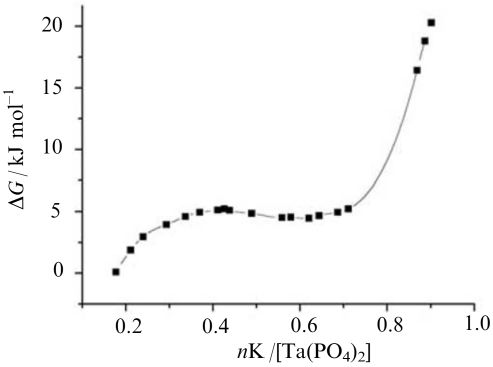

Figure 1 Dependence of ΔG on the degree of substitution for process (1) at 292 K ($M^+ = K^+$).

Based on the proposal proved above, the equation (1) was treated by means of commonly used ion-exchange equilibrium constants:

$$K = [M_{\underline{s}}^+][H_{\underline{l}}^+]/[H_s^+][M_l^+] \qquad (3)$$

At low concentrations we could use concentrational equilibrium constants in the determination of the thermodynamic parameters of this process. Based on the calculated equilibrium constants values of Gibbs energies were determined. The plot of ΔG *vs.* the degree of proton substitution at 292 K ($M^+ = K^+$) is reproduced in Figure 1. That part of the curve with a low degree of exchange was obtained by means of exchange reactions between acid tantalum phosphate and KCl solutions of various concentrations. For all of the processes under investigation it is possible to divide the curve into three parts of varying steepness. When the degree of substitution is less than 0.1 or more than 0.9–0.95 the value of the equivalent constant decreases sharply because of growth in the configuration entropy according to the advantage of a contamination of a basic substance with a trace impurity of the other one. The interval between these two degrees of substitution is characterized by a continuous increase in the equilibrium constant and a decrease in ΔG. This is caused by a correction of the interlayer spacing with cation uptake. The uptake of cations into the bulk of the crystals leads to a modification of their structure. This facilitates the further diffusion of cations into the matrix and results in a decrease in ΔG. After the calculation of ΔG values for reactions at

Table 1 Thermodynamic parameters for the ion-exchange processes in acid tantalum phosphate for 50% degree of substitution.

Exchanging cations	ΔH / kJ mol^{-1}	ΔS / J mol^{-1} K^{-1}
H^+/Li^+	-35 ± 3	-130 ± 7
H^+/Na^+	-36 ± 6	-140 ± 20
H^+/K^+	$+8 \pm 5$	$+12 \pm 8$

different temperatures the values of the enthalpy and entropy were estimated. It is therefore sensible to compare values obtained at the same degrees of substitution. Values given in Table 1 are related to 50% degree of substitution.

After the titration experiments all the precipitates were filtered off, dried out and investigated by means of thermogravimetry (speed of heating 10 K min^{-1}) and X-ray diffraction. Based on weight loss the compositions of products were established; these are: $HTa(PO_4)_2 \cdot 2H_2O$, $LiTa(PO_4)_2 \cdot 2H_2O$, $NaTa(PO_4)_2 \cdot 3.2H_2O$ and $KTa(PO_4)_2 \cdot H_2O$. In the case of $NaTa(PO_4)_2 \cdot 3.2H_2O$ the degree of hydration was not constant ($3 < n < 3.5$). An X-ray diffraction study showed monoclinic symmetry with β ranging from 92 to 95.5°. The sodium compound proved to be a mixture of two phases: $NaTa(PO_4)_2 \cdot 3H_2O$ and $NaTa(PO_4)_2 \cdot 3.5H_2O$.

The cation-exchange process for acid tantalum phosphate in solutions has been studied for the first time in this publication. It was shown that the ion-exchange process leads to the formation of solid solutions $M_xH_{1-x}Ta(PO_4)_2 \cdot nH_2O$. An evaluation of thermodynamic parameters was made.

References

1 A. Clearfield, *Chem. Rev.*, 1988, 125.
2 I. V. Tananaev, I. A. Rozanov, K. A. Avduevskaya, A. N. Beresnev and V. R. Berdnikov, *Fosfaty chetyrekhvalentnykh elementov* (*Phosphates of tetravalent elements*), Nauka, Moscow, 1972 (in Russian).
3 A. Clearfield, *Materials Chemistry and Physics*, 1993, **35**, 257.
4 A. B. Yaroslavtsev, Z. N. Prozorovskaya and V. F. Chuvaev, *Zh. Neorg. Khim.*, 1990, **35**, 1379 (*Russ. J. Inorg. Chem.*, 1990, **35**, 780).
5 R. Llavona, M. Suarez, J. R. Garcia and J. Rodriguez, *Inorg. Chem.*, 1989, **28**, 2863.
6 A. B. Yaroslavtsev, Z. N. Prozorovskaya and V. F. Chuvaev. *Zh. Neorg. Khim.*, 1990, **35**, 1100 (*Russ. J. Inorg. Chem.*, 1990, **35**, 619).
7 A. B. Yaroslavtsev and A. E. Nikolaev, *Mendeleev Commun.*, 1995, 137.
8 N. G. Chernorukov, T. V. Sharova, A. I. Kryukova and I. A. Korshunov, *Zh. Neorg. Khim.*, 1985, **30**, 1177 (*Russ. J. Inorg. Chem.*, 1985, **30**, 665).
9 G. Alberti, *Acc. Chem. Res.*, 1978, **11**, 163.

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