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EXPERIMENTAL AND PREDICTED ISOELECTRIC POINTS FOR NIOBIUM AND VANADIUM PENTOXIDE

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ABSTRACT

The isoelectric points for niobium and vanadium pentoxides were determined through electrophoretic measurements and the experimental results were compared with three alternative procedures to predict this parameter. Experimental and predicted results show good agreement for Nb_2O_5 that presents a well defined value for the isoelectric point but they do not correlate well in the case of V_2O_5 that presents a rather high solubility in the isoelectric pH region.

RESUMO

Os pontos isoelétricos de pentóxido de niobio e vanádio foram determinados experimentalmente através de medidas eletroforéticas e comparados com valores calculados teoricamente usando tres métodos diferentes. Para Nb_2O_5, que apresenta um ponto isoelétrico muito bem definido, os valores experimentais concordam muito bem com os valores calculados. Por outro lado, para V_2O_5, que tem uma solubilidade alta na região do pH isoelétrico, a correlação é menos satisfatória.

Key words: Niobium pentoxide, vanadium pentoxide, electrophoresis, isoelectric points.

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INTRODUCTION

The knowledge of the point of zero charge (zpc) or the isoelectric point (iep) of the individual components of complex particulate materials dispersed in aqueous electrolyte solutions permits, in many cases, a characterization of the solids in terms of their surface composition. For the case of supported catalysts for instance, Gil-Llambias et al.[1] developed a method to estimate the apparent surface coverage of the particles by equating the isoelectric point of the catalyst with the weighted average of the iep of each component, i.e., the support and the supported oxide.

Niobium and vanadium pentoxide are extensively used in the preparation of new materials like high electric conductivity or dielectric ceramics[2], support material for metallic catalysts[3] or as catalysts when dispersed on the surface of support oxides like Al_2O_3, TiO_2 or SiO_2[4]. However, there is still very little information available on the surface properties of these oxides, when dispersed in aqueous electrolyte solutions. In this paper, the isoelectric points for Nb_2O_5 and V_2O_5 obtained using electrophoretic measurements are reported and the experimental results are compared with the predicted values obtained using three different procedures to estimate this parameter theoretically.

EXPERIMENTAL PROCEDURE

Two samples of niobium pentoxide were used in this work. One of them was prepared by calcination of niobic acid (Nb_2O_5 x nH_2O) at 550°C. Through X-ray diffraction, the solid was identified as Nb_2O_5 presenting a monoclinic structure. The sample was polydisperse containing particles from 1 to 100 µm in diameter and a surface area of 34 m^2g^{-1}. The other sample was kindly supplied by the Companhia Brasileira de Metalurgia e

Mineração and presented an orthorhombic structure. This preparation was fairly monodisperse, containing predominantly 1 µm particles and a surface area of 3 m^2g^{-1}. The vanadium pentoxide was a commercial sample obtained from Merck and presented an orthorhombic structure. Most of the particles were 2 µm in diameter but a small fraction presenting sizes up to 20 µm was also present. The BET surface area for this oxide was 4 m^2g^{-1}. Copper oxide was an analytical grade commercial sample obtained from Merck, Al_2O_3 was obtained from Catalysts Chemical Industry (CCI, USA) and Fe_2O_3 was a sample of pure mineral produced in the region of Minas Gerais, Brazil.

Water was deionized using a Millipore Milli-Q columns system and its resistivity was about 10 MΩ.cm. Potassium nitrate, nitric acid and sodium hydroxide were reagent grade products and were used without further purification.

The electrophoresis of the solid particles was measured using an electrophoresis apparatus provided with a thin walled cylindrical cell (Rank Bros. UK). The polarity of the electrodes was reversed between consecutive measurements to avoid polarization. The dispersions were prepared in KNO_3 solutions and the pH was modified using HNO_3 and KOH. Mean values resulting from at least twelve measurements for each point were the reported values. For V_2O_5 a few measurements were also carried out using a Malvern Zetasizer IIc particle electrophoresis analyzer; the results obtained using both techniques were practically identical.

RESULTS AND DISCUSSION

Experimental Isoelectric Points

The electrophoretic mobility versus pH diagrams obtained for the two samples of niobium pentoxide in potassium nitrate solutions are presented in Figure 1. The curves were drawn fitting the experimental

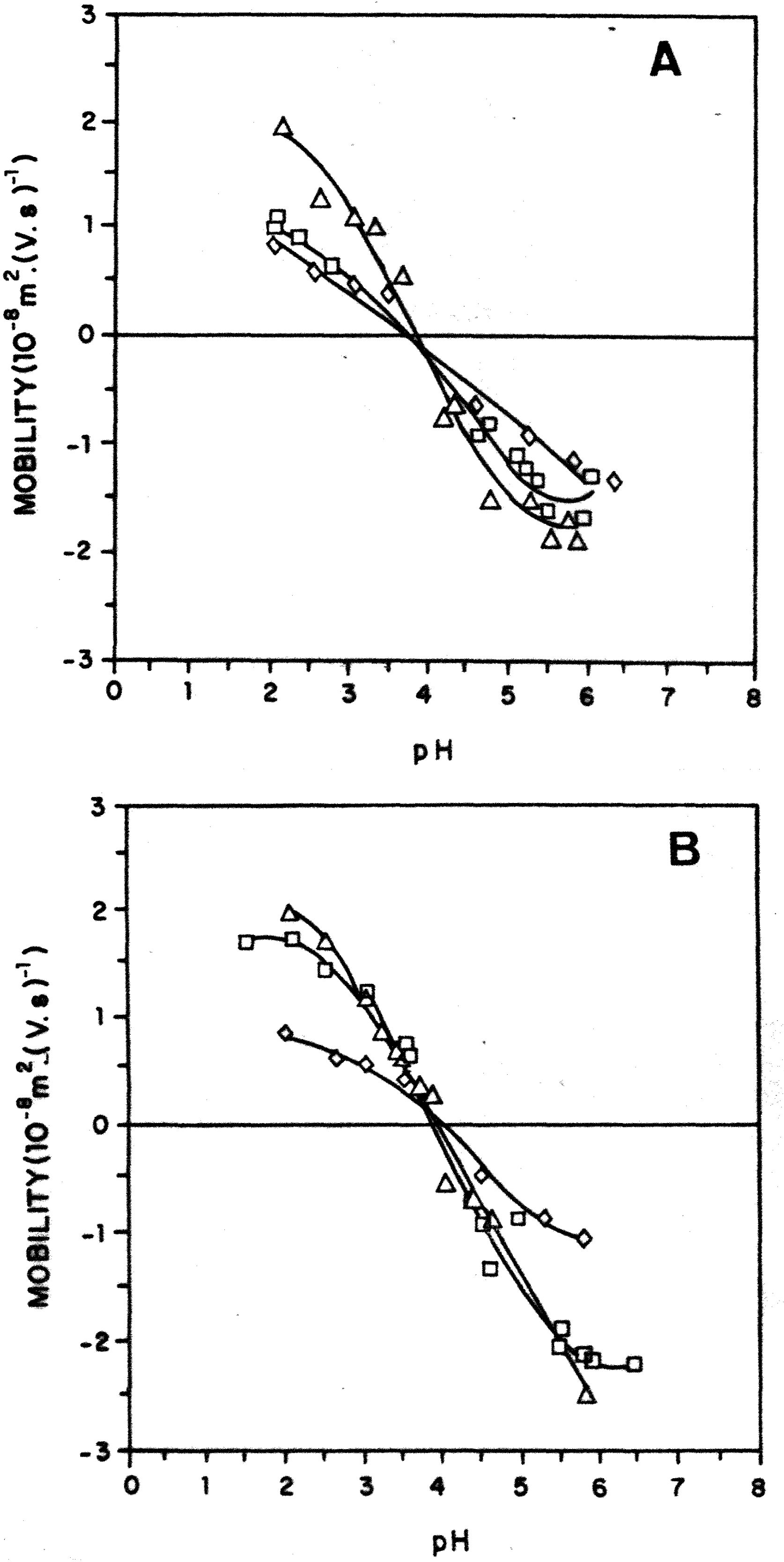

FIG. 1 - Eletrophoretic mobility-pH diagrams for Nb_2O_5 calcinated at 550°C (A) and commercial sample (B) in KNO_3 solution. -Δ- $5x10^{-4}$; -□- $5x10^{-3}$ and -◇- $5x10^{-2}$ mol dm^{-3}.

points to a fourth-order polynomial. For both samples, the electrophoretic mobility is zero at the same pH value for the three electrolyte concentrations employed as expected for particles dispersed in an indifferent electrolyte solution[5]. An isoelectric point of 3.8 was therefore obtained for this oxide.

The behavior of the vanadium pentoxide dispersions was different. The solid particles presented a rather high solubility in acid as well as in alkaline solutions. For this reason, experimental measurements were difficult to carry out in this system due to the high conductivity of the aqueous dispersions. As a result, it was not possible to determine the mobility of particles under low pH conditions, at which positively charged species should be expected to be present, even using the zeta sizer apparatus that detects particles in the submicron range. The experimental results, when extrapolated to low pH values, showed isoelectric points between pH 1 and 1.5 depending on the concentration of electrolyte. The isoelectric point obtained by Gil Llambias[6] for a different sample of V_2O_5 also falls in this pH region. In their study, only one point was presented for positively charged particles, which confirms the experimental difficulties in this pH region. The small increment in the extrapolated iep for higher electrolyte concentration may be attributed to specific adsorption of ions by the solid but may also correlate with the formation of highly charged isopoly-vanadates in solution and its subsequent reprecipitation on the particles as described by Healy for other oxides[7].

Predicted Isoelectric Points

When an insoluble metallic oxide is suspended in water, the hydroxylated surface groups undergo amphoteric dissociation according to the reactions:

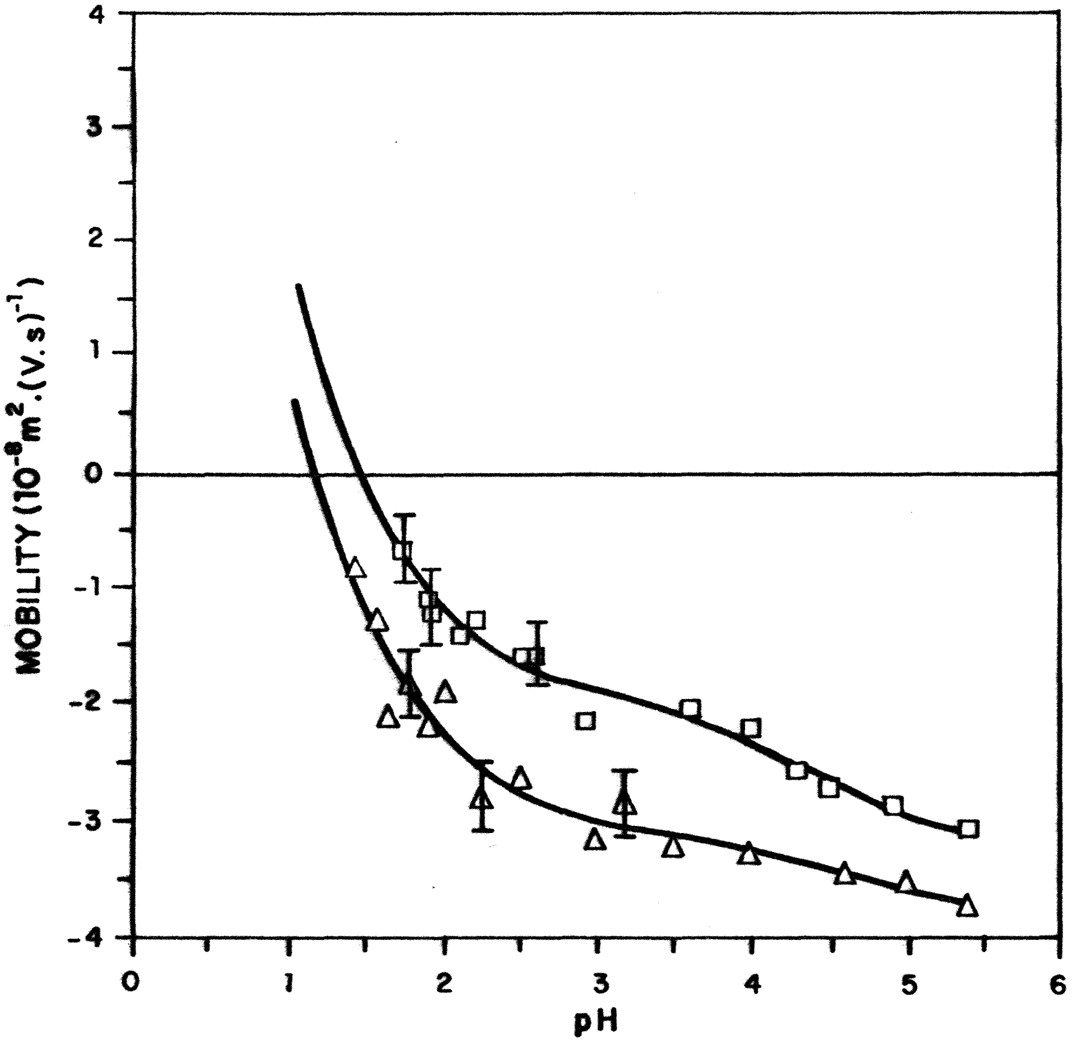

FIG. 2 - Eletrophoretic mobility-pH diagrams for V_2O_5 in KNO_3. -Δ- $5x10^{-4}$ and -□- $5x10^{-3}$ mol dm^{-3}. The points containing deviation bars were obtained using the Zetasizer apparatus.

$$\ldots MOH + H^+ \overset{K_b}{\rightleftarrows} \ldots MOH_2^+$$

$$\ldots MOH \overset{K_a}{\rightleftarrows} MO^- + H^+$$

Where MOH, MOH_2^+ and MO^- are the neutral, positively and negatively charged species on the solid surface and K_b and K_a are the basic and acid dissociation constants, respectively.

At a particular pH value the concentration of positive sites equals the concentration of negative sites. This condition is defined as the point of zero charge[8] which, in the absence of specific adsorption, should coincide with the isoelectric point. From the previous equations, it is possible to show that the point of zero charge may be defined by the following relationship:

$$ZPC = \frac{1}{2}\,(pK_a - pK_b) \qquad (1)$$

A simple method to estimate the point of zero charge for metallic oxides was suggested by Tanaka and Ozaki[9]. They used a parameter called generalized electronegativity of the metal ion, X_i, defined as:

$$X_i = (\delta I/\delta z) \qquad (2)$$

Where z is the charge on the metal ion and I is the ionization potential of the atom. I may be approximately expressed as a quadratic function of z:

$$I = Az + Bz^2 \qquad (3)$$

Obtaining the derivative of I in Equation (3) as:

$$X_i = A + 2Bz \qquad (4)$$

for z = 0, X_i is equal to the Pauling's electronegativity[10] of the neutral atom, X_0, hence,

$$X_i = (1 + 2 \frac{B}{X_0} z) X_0 \tag{5}$$

The ratio B/X_0 was assumed to be unity by the authors and a good linear relationship between pK_a and X_i was obtained. As expected from equation 1, the zpc also correlates with the generalized electronegativity and when all the zpc and iep values compiled by Parks[11] were plotted against this parameter a fair linear correlation was also obtained.

We selected thirteen oxides for which there are reasonably reliable zpc and/or iep data in the literature and calculated the corresponding X_i using the electronegativity values reported by Gordy and Thomas[12], the values are presented in Table I.

The equation obtained by least-squares fitting the data to a straight line (Figure 3) was:

$$ZPC = 14.43 - 0.58 X_i \tag{6}$$

In Table 1 are also presented the zpc values obtained using equation 6. A reasonable agreement is observed between the experimental and predicted data. An equally acceptable agreement was obtained for other oxides not included in Table I.

The electronegativities for niobium and vanadium are 1.7 and 1.9. Introducing these parameters in equation 6, the zpc values of 3.6 and 2.3 are obtained for Nb_2O_5 and V_2O_5, respectively. The results show a good agreement with the experimental data in the case of niobium but the value predicted for vanadium pentoxide is higher than the value obtained from the extrapolation of the experimental data.

One way to improve the predicted results would be to calculate the ratio B/A (or B/X_0 in equation 5) assumed to be one, by Tanaka and Ozaki. This constant may be obtained from the first and second ionization potentials of the metal ion. However, the use of these parameters did not improve the predicted zpc values for these oxides.

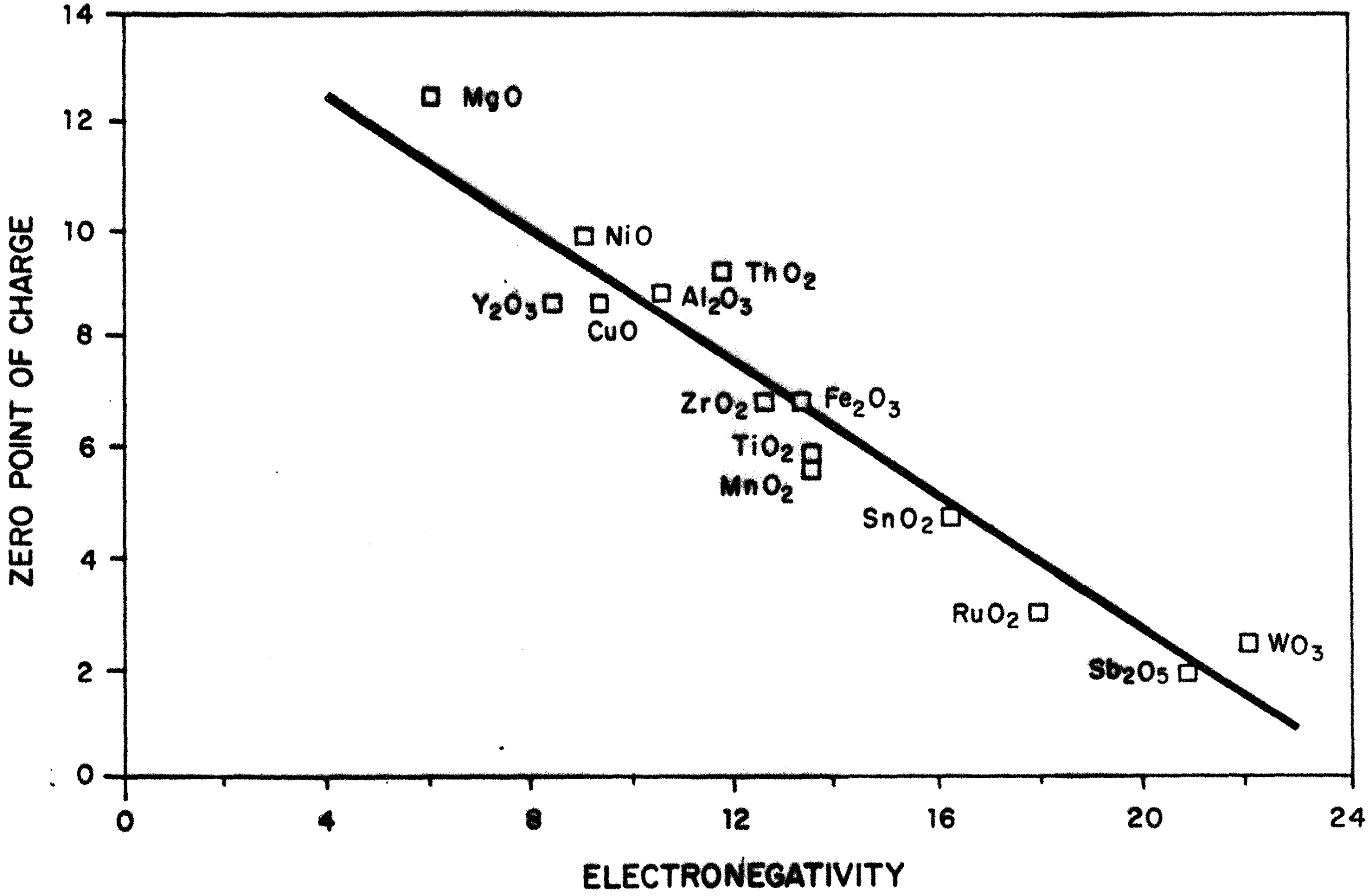

FIG. 3 - Experimental zpc versus generalized electronegativity for several metal oxides.

TABLE I

Points of Zero Charge and Generalized Electronegativity of the Various Oxides Used in Figure 3

Oxide	Experimental zpc	Reference	X_i	zpc predicted by equation 6
WO_3	0.3	13	26.0	-0.5
Sb_2O_5	1.9	14	19.6	3.0
SnO_2	4.7	15	16.2	5.0
RuO_2	5.1	16	18.0	4.0
MnO_2	5.6	17	13.5	6.6
TiO_2	5.8	18	14.4	6.1
Fe_2O_3	6.8	this work	12.6	7.1
ZrO_2	6.8	19	13.5	6.6
CuO	8.5	this work	10.0	8.6
Y_2O_3	8.6	20	8.4	9.0
Al_2O_3	8.8	this work	10.5	8.3
NiO	9.8	21	8.5	9.5
MgO	12.4	22	6.0	11.0

An alternative procedure to predict isoelectric points was introduced by Parks[11] and further developed, more recently, by Yoon et al.[23]. The authors used a model similar to that already described for the amphoteric dissociation at the mineral surface and derived an expression for the free energy involved in the process of approaching two protons to the metal oxide. The equation obtained for the zero point of charge was:

$$ZPC = 18.43 - 53.12\ \left(\frac{\nu}{L}\right) - \frac{1}{2}\log\left(\frac{2-\nu}{\nu}\right) \qquad (7)$$

Where ν represents the charge on the metal ion divided by its coordination number in the oxide, L is the distance between the metal ion and the proton in the protonated oxide, defined as the O-H distance in the ice (1.01 Å) plus the M-O distance in the oxide crystal. The numerical constants in equation 7 were calculated by the authors using 12.4 and 9.1, respectively, for the zpc of MgO and α-Al_2O_3 and the corresponding crystallographic metal-oxygen distances in these oxides.

Niobium pentoxide presents octahedral coordination with a niobium oxygen distance of 1.95 ± 0.01 Å and a coordination number of 6[24]. When this data were introduced in equation 7, a value of 3.4 was obtained for the zpc of Nb_2O_5. Vanadium pentoxide has an orthorhombic structure with a coordination number of 5. The V-O distance reported by Wickoff[25] is between 1.54 and 2.02 Å and the values 1.93, 1.97, 1.95 and 1.67 Å were reported by Pope and Dale[26] for the five V-O bonds. Using these data, predicted values in the range -2.4 to 0.9 were obtained for the iep of V_2O_5. Therefore, the predicted value for V_2O_5 in this case was lower than the iep's obtained by the extrapolation of the experimental electrophoretic mobility data, but a good fit was obtained for Nb_2O_5.

A third method to estimate the point of zero charge of oxides was also introduced by Parks[8] and subsequently applied to oxides[27] and to salt type minerals[28]. The partial dissolution of the oxide results in the formation of metal hydroxy complexes in solution presenting different charges. When the free energies of formation for these species are known, it is possible to draw a diagram showing the logarithm of the concentration of the different species as a function of pH. The isoelectric point of the solution is defined as the pH at which the concentration of the two oppositely charged dominant ionic species of the same central ion, are equal. Considering that the solution is in equilibrium with the solid-solution interface it seems reasonable to assume that this pH also corresponds to the isoelectric point (or point of zero charge) of the solid.

Table II presents the free energies of formation for a few hydroxo complexes for niobium (V) and vanadium (V) ions[29,30].

Using these data, it was possible to plot the log concentration - pH diagrams presented in Figures 4 and 5. The zpc's for Nb_2O_5 and V_2O_5 obtained using this method were 3.4 and 2.2, respectively. There are several different negatively charged species in the alkaline pH, specially in the case of vanadium, however they do not affect the determination of the iep by this procedure.

TABLE II

Free Energy of Formation for Some Hydroxo-Complexes of Pentavalent Niobium and Vanadium[29,30]

Compound	ΔG_f (kcal.mol^{-1})
Nb_2O_5 $_{(s)}$	-422.6
$Nb(OH)_4^+$ $_{(aq)}$	-288.9
NbO_3^- $_{(aq)}$	-222.8
$Nb(OH)_5$ $_{(aq)}$	-346.1
V_2O_5 $_{(s)}$	-339.3
VO_2^+ $_{(aq)}$	-140.3
$H_3V_2O_7^-$ $_{(aq)}$	-445.5
H_3VO_4 $_{(aq)}$	-248.6
$H_2VO_4^-$ $_{(aq)}$	-244.0
$H_2V_{10}O_{28}^{4-}$ $_{(aq)}$	-1847.3

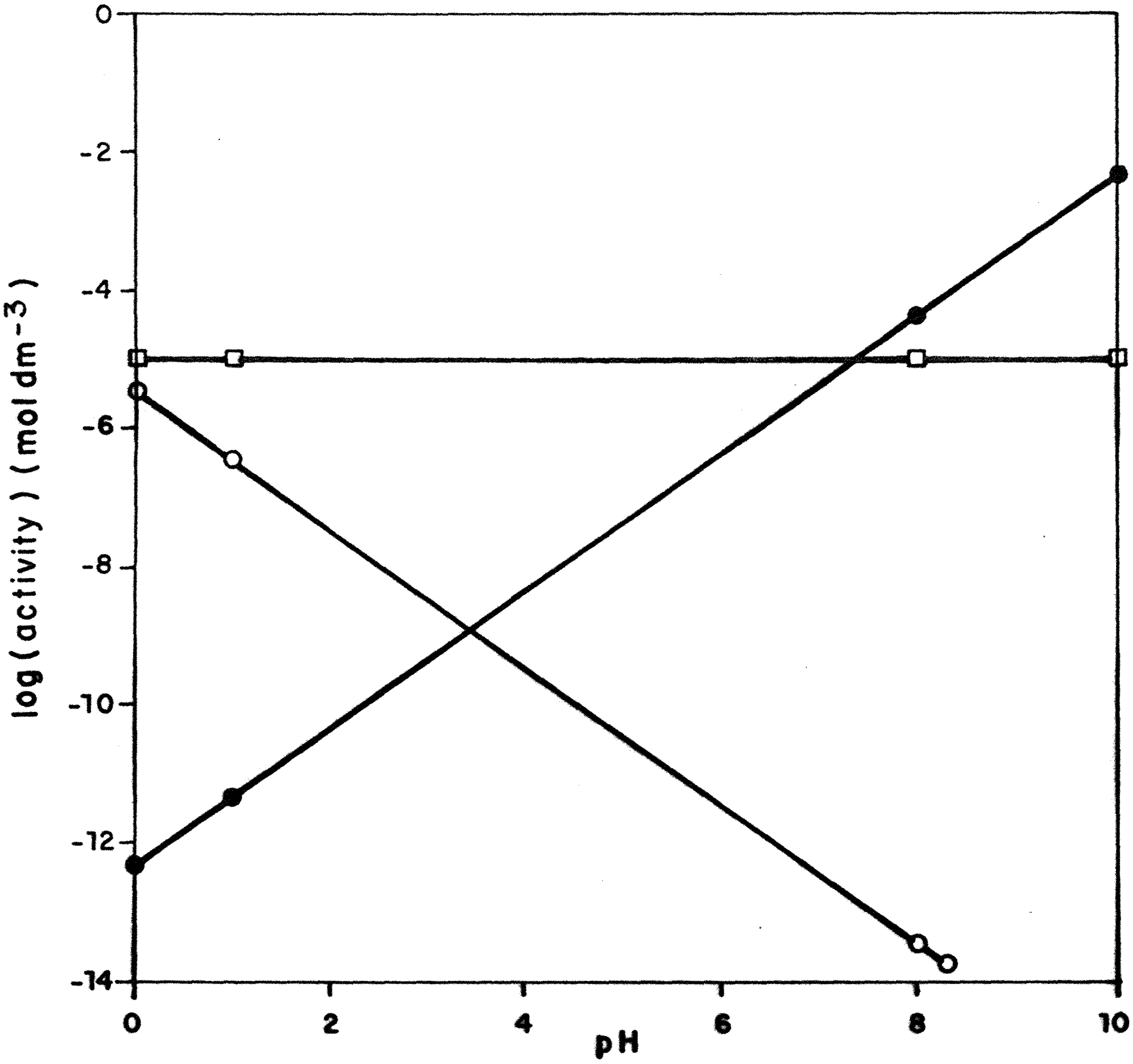

FIG. 4 - Logarithm of activity versus pH for Nb^{+5} dissolved species in equilibrium with Nb_2O_5 -□- $Nb(OH)_5$; -o- $Nb(OH)_4^+$; -●- NbO_3^-.

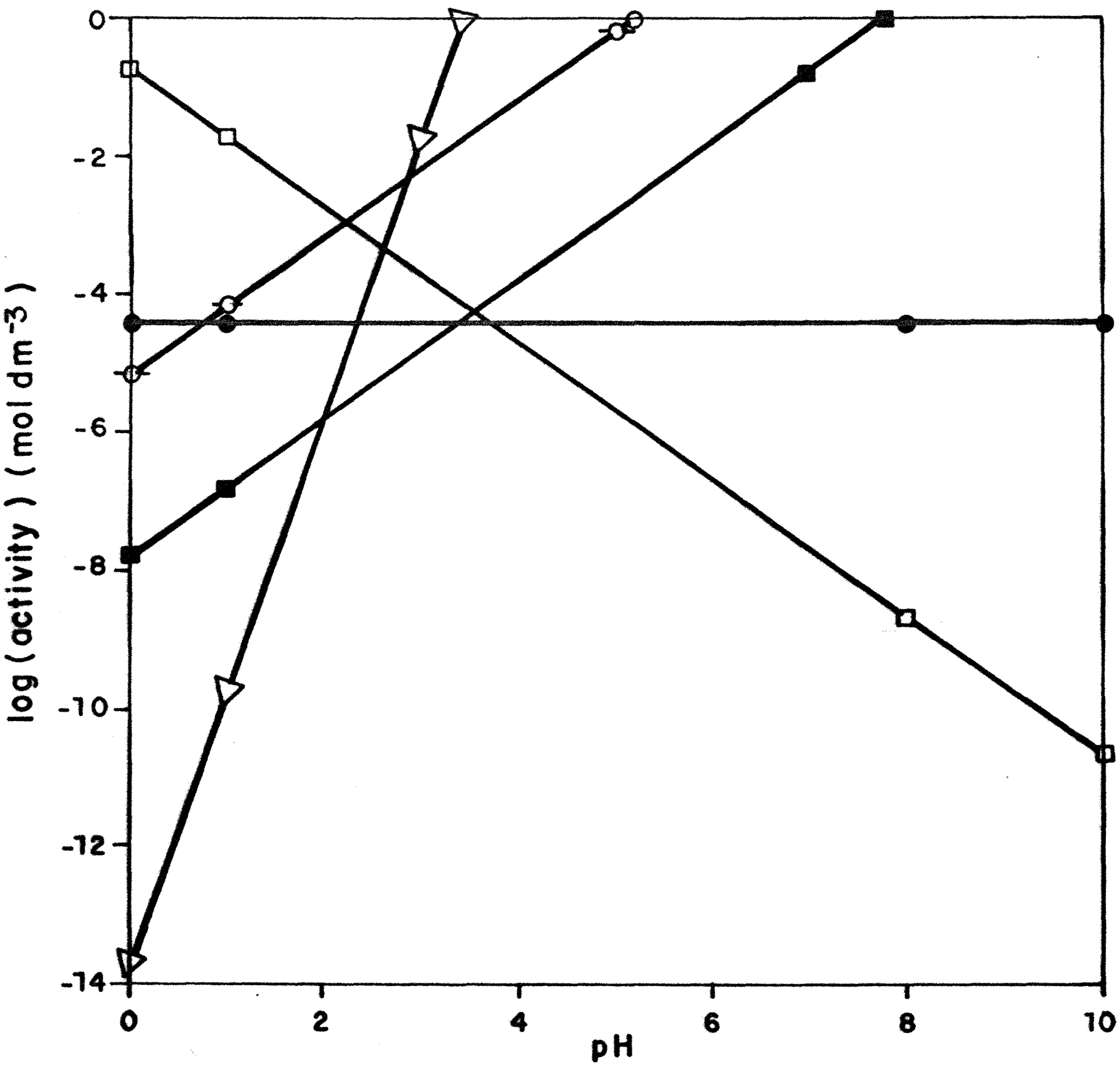

FIG. 5 - Logarithm of activity versus pH for V^{+5} dissolved species in equilibrium with V_2O_5 -□- VO_2^+ -o- $H_3V_2O_7^-$; -●- H_3VO_4; -■- $H_2VO_4^-$; -∇- $H_2V_{10}O_{28}^{-4}$.

TABLE III

Experimental and Predicted Isoeletric Points for Niobium and Vanadium Pentoxide

	Nb_2O_5	V_2O_5
Experimental values:	3.8	≅ 1.5*
Predicted values, method:		
Electronegativities:	3.6	2.3
Crystallographic data:	3.4	-2.4 to 0.9
Thermodynamic data:	3.5	2.3

* Extrapolated value

Table III summarizes the experimental isoelectric points as well as the values obtained by the three alternative procedures used to predict this parameter. It may be concluded that the experimental value obtained for niobium pentoxide i.e. 3.8, shows good agreement with the predicted values. For vanadium pentoxide it was not possible to obtain a well defined iep due, most likely, to an ill-defined interface caused by the high solubility of this oxide in the isoelectric pH region. The extrapolated values were around pH 1.5 and the correlation with the predicted values was less satisfactory in this case. It is interesting also to emphasize that the simplest predicting procedure, using the generalized electronegativity, conduces to results equivalent to those obtained using other more elaborated procedures.

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