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Physico–chemical behaviour of V(V) in a concentrated phosphoric acid

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Abstract

Tests show that the conductivity and viscosity of solutions of phosphoric acid (54% P_2O_5) change as increasing quantities of vanadium are added, indicating that the metallic cation interacts with the phosphoric acid molecule. This behaviour is confirmed by measurements of acidity. Determination of R_0(H) shows that the acidity of the environment increases as a function of the concentration of V(V), suggesting that the interaction between the vanadium and the phosphoric acid molecule releases H^+ protons.

Spectrophotometric measurements are used to determine the type of interaction, the nature of the species resulting from the interaction between the vanadium and the phosphoric acid molecule, and the number of protons involved.

Keywords: Phosphoric acid acidity; Vanadium; Spectrophotometry; Conductivity; Viscosity

1. Introduction

Phosphoric acid is an important intermediary with numerous applications in the synthesis of fertilisers and the production of pure chemicals for use in the food industry and in surface treatments [1–4], for which phosphoric acid of very high purity is increasingly required [5]. Recovery of valuable elements (such as uranium, vanadium, rare earths, etc.) and elimination of harmful components (such as cadmium, molybdenum or lead) from industrial phosphoric acid [6–8] is generally carried out by liquid–liquid extraction or by precipitation [3–5,9]. It is important to understand the way these impurities behave in phosphoric environments so that they can be removed or recovered as efficiently as possible.

In this paper, we present the results of a study we carried out into the behaviour of vanadium (V) in concentrated phosphoric acid, involving the following:

- measurement of conductivity and viscosity;
- determination of the acidity of the phosphoric environment and changes in acidity in the presence of the vanadium cation (V(V));
- investigation by spectrophotometric measurements.

2. Experimental method

Conductivity and viscosity were measured using a Tacussel CD 810 conductivity meter and a Haake Rotovisco RV 100 viscosity meter, respectively.

A Volta Lab PGZ 100 potentiostat controlled by a microcomputer using Volta Master 4 software and an Inolab ion meter were used to determine R_0(H) acidity.

A Helios γ UV–vis spectrometer controlled by Vision 32 software was used for spectrometric measurements.

Vanadium V(V) was added to the solution in the form of V_2O_5. Chemicals used were of analytical quality.

3. Results and discussion

3.1. Study of solution conductivity and viscosity

Measurements of conductivity and viscosity of a solution of phosphoric acid (54% P_2O_5) containing increasing quantities of V(V) are shown in Fig. 1.

Fig. 1 shows that conductivity increases as the concentration of vanadium increases, reaching a peak at a concentration of 5×10^{-3} M of vanadium, after which it declines. Within the range of concentrations studied, the conductivity of the solution is always higher than that of phosphoric acid without vanadium. Viscosity decreases, reaching a minimum at a concentration of

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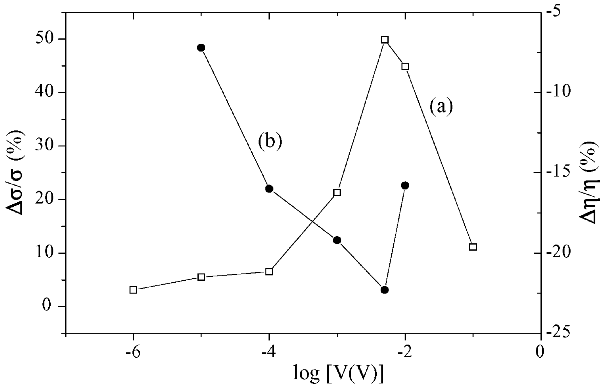

Fig. 1. Evolution of (a) conductivity (σ) and (b) viscosity (η) of phosphoric acid (54% P_2O_5) with concentration of V(V).

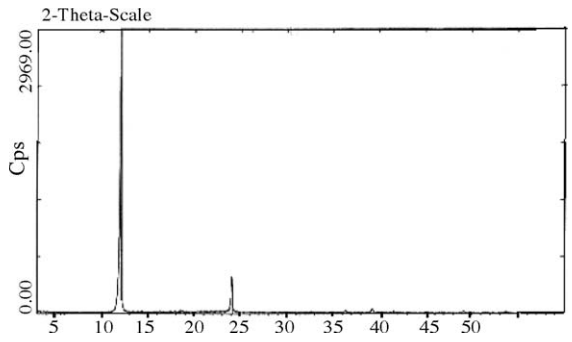

Fig. 2. X-ray diffraction spectrum of the precipitate $VOPO_4{\cdot}2H_2O$.

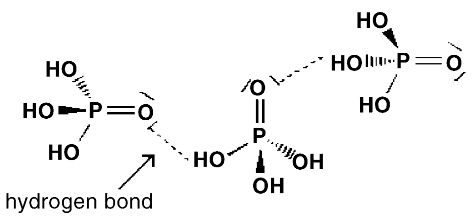

Fig. 3. Representation of the pseudo-macromolecule of phosphoric acid.

Table 1
Acidity of the phosphoric acid (54% P_2O_5) at different concentrations of V(V)

[V(V)] (mol/L)	R_0(H)
0	−6.24
10^{-5}	−6.58
10^{-4}	−6.68
10^{-3}	−6.86
5×10^{-3}	−7.03
10^{-2}	−6.75

5×10^{-3} M of vanadium, and then increases. The viscosity of the solution is always lower than that of phosphoric acid without vanadium. Maximum conductivity and minimum viscosity coincide with the appearance of a precipitate, which X-ray analysis showed to be $VOPO_4{\cdot}2H_2O$ (Fig. 2).

Plotting conductivity against the concentration of V(V) ions (Fig. 1a) shows that, with the concentration of phosphoric acid studied, variation in conductivity is relatively significant (up to 50%) and can be attributed solely to the effect of adding the vanadium salt (V_2O_5). This is confirmed by the plot of viscosity against concentration of the V(V) ion (Fig. 1b).

The viscous character of concentrated phosphoric acid is due to the hydrogen bonds between the H_3PO_4 molecules [10]. These produce pseudo-macromolecules (Fig. 3) of large size (intensified viscous character) which limit the movement of the H^+ ions, reducing the conductivity of the solution.

It is probable that adding vanadium ions to the solution leads to interactions between the vanadium ions and the molecules of phosphoric acid, whereby a compound forms between V(V) and the phosphate species, destroying the hydrogen bonds, reducing the size of the pseudo-macromolecules (leading to a reduction in viscosity) and probably releasing H^+ protons which are more mobile than V(V) (leading to an increase in conductivity).

In order to check this hypothesis (release of H^+ protons resulting from the presence of V(V)), we carried out R_0(H) measurements in order to monitor the way the acidity of the environment changes with the concentration of V(V).

3.2. Determination of the acidity of the phosphoric environment as a function of the concentration of vanadium

The acidity of the concentrated phosphoric environment was measured by determining R_0(H) in accordance with the Strehlow hypothesis [11]. The ferrocene/ferricinium pair ($F_c{}^+/F_c$) was taken as the redox indicator and the quinone/hydroquinone pair (Q/H_2Q) as the pH indicator. R_0(H) was determined using simple potentiometric measurements, taking the system ($F_c{}^+/F_c$) as the comparison. R_0(H) acidity is related to measurements of potential by the following equation [3]:

$$R_0(\mathrm{H}) = \frac{E^{\mathrm{H_2O}}(\mathrm{Q/H_2Q}) - E^{\mathrm{H_2O-acid}}(\mathrm{Q/H_2Q})}{0.058} \qquad (1)$$

where $E^{H_2O}(Q/H_2Q)$ represents the potential of the system (Q/H_2Q) measured in water and $E^{H_2O-acid}(Q/H_2Q)$ represents the potential of the system (Q/H_2Q) measured in the phosphoric acid solution. These potentials are expressed in relation to the system $F_c{}^+/F_c$.

We measured the R_0(H) of solutions of pure phosphoric acid at 54% of P_2O_5 containing different concentrations of vanadium V(V). Results are given in Table 1.

Examination of the results in Table 1 shows firstly that the acidity of the phosphoric acid solution when it does not contain V(V) is comparable to that given in the literature [3] and secondly that the acidity of the environment rises significantly as the concentration in V(V) increases. This increase in acidity reflects the increasing number of free protons in the solution. These free protons, which are more mobile, appear after V(V) ions is added to the concentrated phosphoric acid solution. They probably arise from the interaction of V(V) with the molecules of phosphoric acid. This confirms the hypothesis put forward during the study of conductivity and viscosity.

In order to obtain more information on the interaction which might be occurring between the V(V) ions and the phosphate species in the phosphoric acid environment, we carried out spec-

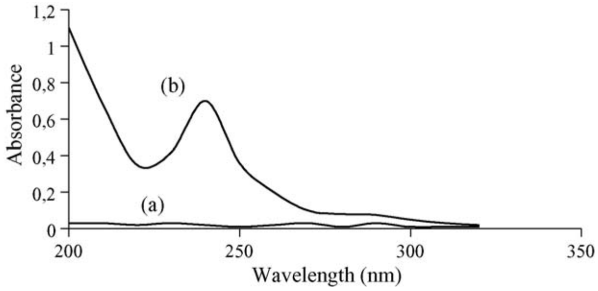

Fig. 4. Spectrum of a solution HCl 2 M without (a) and with 10^{-3} M V(V) (b).

trometric tests (UV–vis) in the environment with and without V(V).

3.3. Spectrophotometric study

As a first step, we carried out spectrophotometric measurements in an environment containing V(V) but not containing any phosphate species. For this, we used a solution of hydrochloric acid. The UV–vis spectra of a solution of hydrochloric acid in the presence and absence of V(V) are shown in Fig. 4. Examination of the spectrum (Fig. 4b) shows an absorption peak at $\lambda = 240$ nm. The intensity of this peak increases with the increasing concentration of V(V), and can therefore be attributed to the presence of the latter in the solution.

When phosphoric acid is substituted for hydrochloric acid, the absorption peak at $\lambda = 240$ nm (corresponding to free V(V) in solution) disappears and is replaced by a new peak at $\lambda = 301$ nm (Fig. 5). For a given concentration of V(V), the position of the new peak is not affected by the concentration of H_3PO_4 in the range of concentrations studied (0.5–12 M). The appearance of the new absorption peak when HCl is replaced by H_3PO_4 shows that there is an interaction between V(V) and the phosphate species. This type of interaction (probably the formation of a coordination compound) is the same throughout the range of concentrations of phosphoric acid studied, indicating that the compound which results from the interaction between the phosphate ions and the V(V) is the same whatever the concentration of phosphoric acid. In order to simplify tests, we chose to continue our investigations on a solution of phosphoric acid at a relatively low concentration.

This interaction between the vanadium (V) and the phosphoric acid molecules results in the formation of a compound accompanied by the displacement of the H^+ protons, which can be represented as follows:

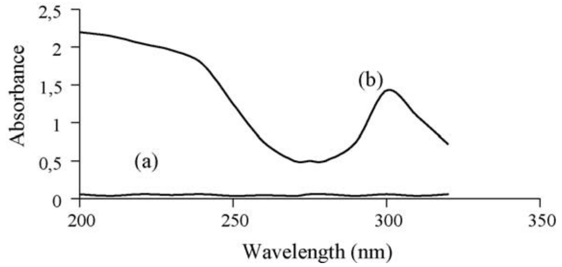

Fig. 5. Spectrum of a solution of H_3PO_4 0.5 M without (a) and with 10^{-3} M V(V) (b).

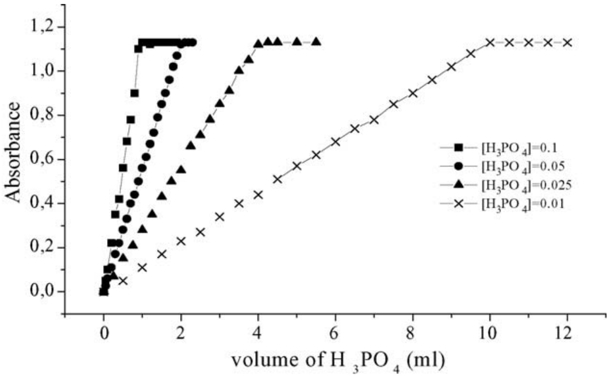

Fig. 6. Absorbance as a function of volume of phosphoric acid added.

$$nM + mL \Leftrightarrow M_nL_m + zH^+ \tag{2}$$

where M represents the metallic cation, L the complexing agent and M_nL_m is the complex formed.

The stability constant of the complex is defined by:

$$K_{nmz} = \frac{[M_nL_m][H^+]^z}{[M]^n[L]^m} \tag{3}$$

or

$$\frac{K_{nmz}}{[H^+]^z} = K'_{nmz} = \frac{[M_nL_m]}{[M]^n[L]^m} \tag{4}$$

where K'_{nmz} is the conditional stability constant and is related to the pH of the solution by the following equation:

$$\log K'_{nmz} = \log K_{nmz} + z\mathrm{pH} \tag{5}$$

3.3.1. Determination of the stability constant of the coordination compound

The stability constant of the vanadium–phosphate complex was determined using direct photometry. To a given volume ($V = 50$ mL) of a solution containing a given concentration of V(V) (10^{-3} M) at fixed pH (buffer solution), we added increasing quantities of phosphoric acid solution with known concentration. At the same time, we monitored the evolution of the absorbance of the resulting solution at $\lambda = 301$ nm. Results are shown in Fig. 6. This graph shows that as known quantities of phosphoric acid are added, absorbance increases, reaching a maximum after which it stabilises. This stability indicates that all the V(V) ions initially present in the solution have reacted with the phosphate ions added. For the same volume and the same concentration of V(V) in the solution, full absorbance is reached more rapidly if a higher concentration of phosphoric acid is used.

At a concentration of 10^{-3} M of V(V) and 10^{-2} M phosphoric acid, maximum absorption is reached when 10 mL of acid has been added to 50 mL of the solution of V(V). This makes it possible to determine the molar ratio of phosphorus/vanadium involved in the reaction. Results obtained for the different concentrations of phosphoric acid used correspond to the same molar ratio of $n(P)/n(V) = m/n = 2$. We can, therefore, say that

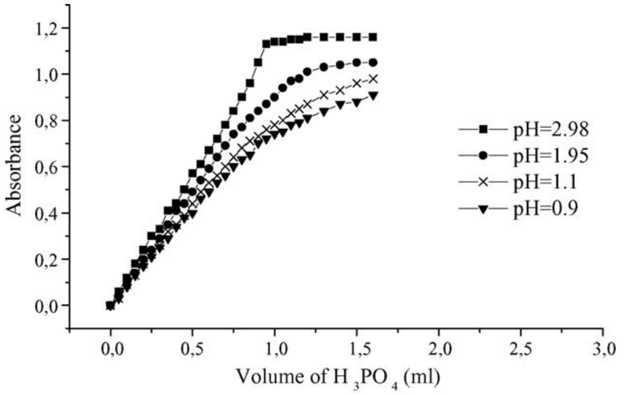

Fig. 7. Absorbance as a function of the volume of phosphoric acid added at different values of pH.

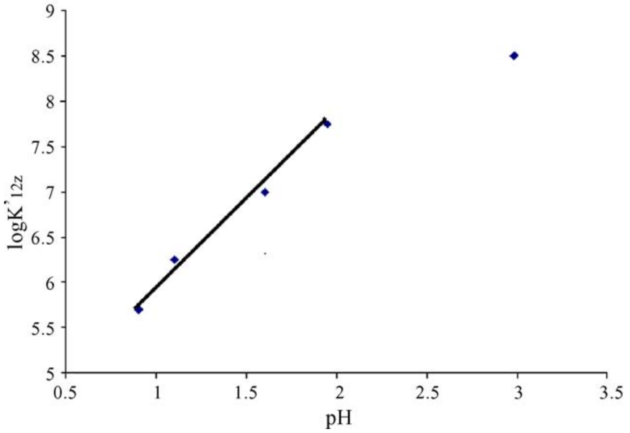

Fig. 8. $\log K'_{12z}$ as a function of pH.

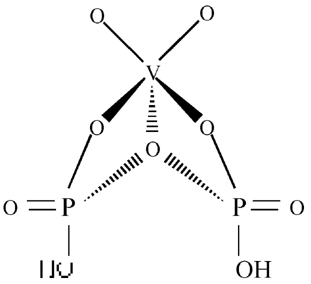

Fig. 9. Probable structure of the complex formed.

under the conditions of the experiment, V(V) forms a compound with two phosphate species ($n = 1$ and $m = 2$, K'_{12z}).

Computer analysis of the results in Fig. 6 using an appropriate program [12,13] gave a conditional stability constant K'_{12z} of 5×10^6. This constant depends on the operating conditions and in particular on the acidity of the environment (see reaction (2)).

The compound formed by the interaction between the vanadium and the phosphate ions contains twice as many moles of phosphorus as of vanadium. The value of the constant is relatively high. The compound, is therefore, stable.

3.3.2. *Study of the influence of pH on K'_{12z}*

We know that

$$K'_{12z} = \frac{K_{12z}}{[H^+]^z} \quad (6)$$

or

$$\log K'_{12z} = \log K_{12z} + z\text{pH} \quad (7)$$

In theoretical terms, the relation between log K'_{12z} and pH is a linear one. To verify this in practice, we carried out experiments similar to those shown in Fig. 6 but over a range of different values of pH (concentration of H_3PO_4 was fixed). Results are shown in Fig. 7. Maximum absorbance depends upon the value of the pH of the solution, showing that K'_{12z} varies as a function of pH.

Fig. 8 shows for pH < 2 that K'_{12z} follows a linear development as a function of pH. The slope of the straight line represents the value of z, which is equal to 1.98; in other words, $z = 2$. Complexation of V(V) by phosphoric acid thus corresponds to the release of two H^+ protons.

This demonstration of the release of the H^+ proton following the formation of a coordination compound involving the V(V) and the phosphate species confirms the results of the measurements of conductivity and R_0(H) acidity.

The conditional stability constant of the compound is shown to increase as the pH of the solution rises (Fig. 8). If this trend is repeated in a concentrated solution of phosphoric acid, the compound formed would be less stable. But this extrapolation should be treated with caution since, in a concentrated solution, the coefficient of activity of the species present in the environment in general and of those involved in the complexation reaction falls below one. Their influence on the characteristics of the reaction should be taken into consideration. Determination of the coefficient of activity of the species concerned would allow a more accurate estimate of the conditional stability constant involved in the formation of a coordination compound between vanadium and the phosphate species in a concentrated solution of phosphoric acid.

Consequently:

- in the light of the spectrophotometric results;
- given that according to the literature [14], V(V) occurs as $VO_2{}^+$ in a concentrated acid environment;
- given that one V(V) bonds with two phosphate species in the complexation reaction, leading to the release of two protons;
- in view of studies of the speciation of V(V) in an acidic environment and its interaction with other acids [15],
- the probable structure of the complex arising from the interaction between V(V) and the phosphate species in a phosphoric acid environment can be represented in Fig. 9. The most likely complexation reaction, can therefore, be written:

$$VO_2(H_2O)^+ + 2H_3PO_4 \leftrightarrow VO_2O(PO_3H)_2{}^{1-} + 2H_3O^+ \quad (8)$$

4. Conclusion

We used measurements of conductivity, viscosity and R_0(H), together with spectrophotometric analysis to show that vanadium ions react with phosphate species to form a coordination compound in the ratio $n(\mathrm{P})/n(\mathrm{V}) = 2$, leading to the release of two H^+ protons. The probable reaction is:

$$VO_2(H_2O)^+ + 2(H_3PO_4) \leftrightarrow VO_2O(PO_3H)_2{}^{-1} + 2H_3O^+$$

The conditional stability constant at pH 1.5 is $K'_{122} = 5 \times 10^6$.

According to our results and to other similar works, the probable structure of the complex formed is proposed in Fig. 9.

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