Formation of monofluorophosphate from fluoride in phosphoric acid – water and phosphoric acid – sulfuric acid – water mixtures

Kenneth E. Newman, Raymond E. Ortlieb, Nicole Pawlik, and Jason Reedyk

Abstract: When dissolved in concentrated phosphoric acid, sodium fluoride reacts rapidly to form monofluorophosphate. In less concentrated acid, the reaction does not proceed to completion, and the reaction kinetics become very much slower. The equilibrium and rate constants for the reaction have been determined. In ternary mixtures of phosphoric acid, sulfuric acid, and water, the formation of monofluorophosphate is considerably enhanced, and the kinetics are rapid. The results are interpreted in terms of the very low water activity coefficients in strong-acid solutions.

Key words: monofluorophosphate, monofluorophosphoric acid, ^{19}F NMR, ^{31}P NMR, phosphoric acid, sulufric acid, equilibria, kinetics.

Résumé : Lorsqu'il est dissout dans de l'acide phosphorique concentré, le fluorure de sodium réagit rapidement pour former le monofluorophosphate. Dans de l'acide moins concentré, la réaction n'est pas complète et la cinétique de la réaction est ralentie. On a déterminé les constantes d'équilibre et de vitesse de la réaction. Dans des mélanges ternaires d'acide phosphorique, d'acide sulfurique et d'eau, la formation du monofluorophosphate est très accélérée et la cinétique est rapide. On interprète les résultats en fonction des très faibles coefficients d'activité de l'eau dans des solutions fortement acides.

Mots-clés : monofluorophosphate, acide monofluorophosphorique, RMN du ^{19}F, RMN du ^{31}P, acide phosphorique, acide sulfurique, équilibre, cinétique.

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Introduction

Mono-, di-, and hexafluorophosphates, along with their corresponding acids, were first synthesized and characterized by Lange and co-workers in a series of papers starting in 1926 (1). As part of this extended study, they reported that sodium fluoride, when dissolved in concentrated phosphoric acid, gave a mixture of HF and monofluorophosphoric acid (MFP), H_2PO_3F.[2] The ratio of MFP to HF increased with increasing phosphoric acid concentration. The patent literature suggests that sodium monofluorophosphate (Na_2PO_2F) is commercially manufactured using very forcing conditions. For example, the 1993 patent of Swidersky et al. involves mixing H_3PO_4, NaOH, and NaF in stoichiometric amounts, together with a small amount of water, at temperatures between 150 and 400 °C (2). The anhydrous acid itself can be made under much less forcing conditions, namely room temperature reaction of anhydrous metaphosphoric acid (HPO_3) and gaseous hydrogen fluoride (3).

MFP salts find uses in the treatment of osteoporosis, control of corrosion (particularly in steel reinforcing in concrete), and as fungicides and bactericides. However, the major use of MFP salts is as anticaries agents in toothpastes. The hydrolysis of MFP to fluoride is extremely slow at near neutral pH values, although it is hydrolyzed readily by phosphatase enzymes, including those found in saliva (4). The addition of an acid has also been shown to significantly enhance the reaction rate (5).

Phosphoric acid is manufactured by the reaction of the ore (apatite), $Ca_5(PO_4)_3(OH)$, with concentrated sulfuric acid in the temperature range of 70–80 °C (the so-called "wet process") according to the simplified reaction [1] (6).

$$[1] \qquad Ca_5(PO_4)_3(OH) + 5H_2SO_4 = 5CaSO_4(s) + 3H_3PO_4 + H_2O$$

The ore is invariably contaminated with fluoroapatite, $Ca_5(PO_4)_3(F)$, with the total fluoride content of the feedstock in the range of 3.5%–4%. The strongly acidic reaction conditions favor the formation of HF, which dissolves silica and silica-like impurity minerals in the ore. Products of this reaction are various fluorosilicates, including the volatile silicon

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[2] Given the strongly acidic media of interest in this paper, the extent of protonation of monofluorophosphate will not always be obvious. Thus, we will refer to the species as MFP regardless of its form except where noted.

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tetrafluoride (SiF_4), as well as hexafluorosilicic acid (H_2SiF_6) and (or) its salts. Phosphoric acid reactor vessels are thus typically scrubbed to remove the volatile HF and SiF_4. The other product of reaction [1], calcium sulfate (gypsum) is typically pumped as a slurry to tailings ponds; process water is also stored for recycle in storage ponds. These ponds are typically fairly acidic (pH < 2) with very high dissolved solids content, and with fluoride levels in the range of 0.35%–1.35% (7). Probably, the fluoride is mostly in the form of HF and SiF_6^{2-}, but the latter species may partially hydrolyze to SiF_4. Fugitive emissions of gaseous HF and SiF_4 from the ponds are thus of environmental concern.

The work reported here is the first part of an extended study to explore and understand in detail the chemistry and fate of the fluoride impurities as they pass through the "wet process" manufacture of phosphoric acid. The ready formation of MFP in phosphoric acid under benign conditions led us to focus initially on the conditions that determine its formation. Given the central role of sulfuric acid on the manufacturing process, its effect on MFP formation was clearly important to the study.

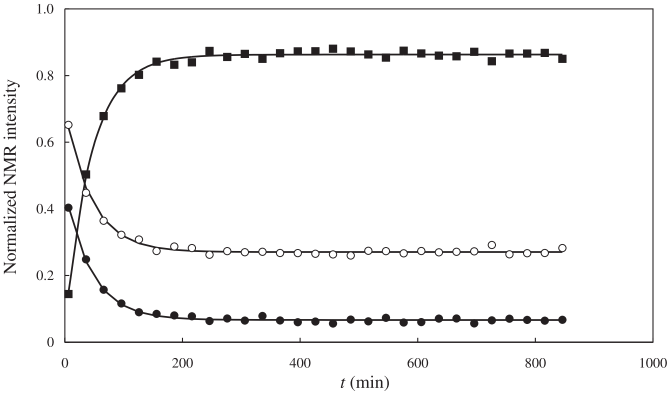
Experimental

NaF (Fisher, ACS grade), Na_2PO_3F (Alfa Aesar, >99%), H_3PO_4 (Aldrich, 100%), H_3PO_4 (Sigma, 85%, ACS), H_2SO_4 (95%–98%, ACS grade), and D_2O (Cambridge Isotope Laboratories, 99%) were used as received. All solutions were prepared by weight in polyethylene or Teflon containers and were typically 0.01 *m* total fluoride. Solutions typically contained 10%–15% D_2O, although a few solutions were prepared with 40%–50% D_2O. Some of the most-acidic solutions were prepared without D_2O and thus were run unlocked. NMR spectra were obtained with a Bruker 400 Avance NMR spectrometer using a Bruker ATMA multinuclear probe operating at 161.98 MHz for ^{31}P and 376.46 MHz for ^{19}F. All NMR spectra were run at 22.0 ± 0.1 °C. Samples were contained in 5 mm NMR tubes with polytetrafluoroethylene – fluorinated ethylene polypropylene copolymer (PTFE–FEP) liners (Wilmad LabGlass, NJ, USA).

Results

The ^{19}F NMR spectrum of a 0.01 *m* solution of NaF in 85%[3] H_3PO_4 solution consists of a doublet, centered at –75.1 ppm with a coupling constant of 937 Hz, and a somewhat broad peak at ~147 ppm. The ^{31}P NMR spectrum of a similar solution consists of a very large peak centered at ~0 ppm, a small doublet centred at –7.4 ppm with a coupling constant of 937 Hz, and another small peak at –12.8 ppm. The spectra are readily interpreted in terms of a mixture of MFP and HF. The doublet feature in each spectrum is due to $J_{12}(^{19}F–^{31}P)$ coupling in the MFP. The large peak at ~0 ppm in the ^{31}P spectrum is due to H_3PO_4, and the small peak at –12.8 ppm is due to a small amount of pyrophosphate ($P_2O_7^{4-}$). These assignments are consistent with literature values (8). It is worth noting that the ^{19}F chemical shifts of both MFP and HF and the MFP coupling constant show considerable variation, as the phosphoric acid concentration is varied from 5% to 85% H_3PO_4.

Fig. 1. Variation of normalized NMR intensities of each peak of the monofluorophosphate doublet (closed and open circles) and hydrogen fluoride (closed squares) for a 0.0078 *m* of sodium monfluorophosphate solution in a phosphoric acid – water mixture of the composition $x(H_3PO_4) = 0.254$. The D_2O/H_2O fraction was 0.41. For clarity, the data for the component of the MFP doublet represented by the open circles were displaced vertically by 0.2 units. The smooth curves are the fitted values, obtained as described in the text.



We may define α as the fraction of the fluorine-containing species in the form of MFP

$$\alpha = \frac{c_{MFP}}{c_{MFP} + c_{HF}} \qquad [2]$$

where c_i is the concentration (expressed as either molality or molarity). At 85% H_3PO_4, the value of α from the integration of the ^{19}F spectrum is 0.81. As the phosphoric acid concentration is decreased, not only does α decrease, but also the kinetics of interconversion of HF and MFP become surprisingly slow. The dependence of α on phosphoric acid concentration was thus determined as the infinite-time values obtained from a study of the kinetics of the reaction of 0.01 *m* Na_2MFP in aq. phosphoric acid solutions. Figure 1 shows a typical kinetic ^{19}F NMR run. The integrated NMR peak intensities were normalized by dividing through by the sum of the intensities. The normalized intensities were fitted to a first-order kinetic equation by a non-linear least-squares approach, using the "Solver" facility of Microsoft® Excel. Each NMR peak was fitted to a unique time-zero and time-infinity intensity, but with a common value for the rate constant. For H_3PO_4 compositions greater than 80% [$x(H_3PO_4) > 0.42$], the kinetics were too fast to measure by this NMR method, and thus, only the equilibrium values could be measured. For $x(H_3PO_4) < 0.04$, the infinity values for the MFP peaks were too small to be measured reliably and were thus constrained to zero. Although no extended study was performed, the kinetics do not appear to exhibit any strong isotope effects as the D_2O fraction is changed. Figure 2 shows the values of α as a function of $x(H_3PO_4)$. For the two points

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[3] Throughout this work, "% *i*" refers to the weight% of solvent species *i*, calculated excluding the solutes. *x*(*i*) refers to the mole fraction of solvent species *i*, calculated excluding the solutes.

Fig. 2. Equilibrium fraction (α) of monofluorophosphate as a function of the mole fraction of H_3PO_4. ●: Experimental values; ——— : Fitted values (see Discussion for details).

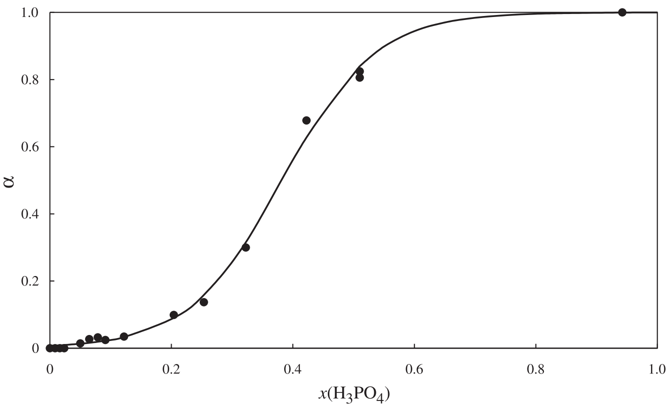


Fig. 3. Apparent first-order rate constants for the interconversion of HF and MFP as a function of the mole fraction of H_3PO_4. The line represents the best straight-line fit, excluding the open-circle data point.

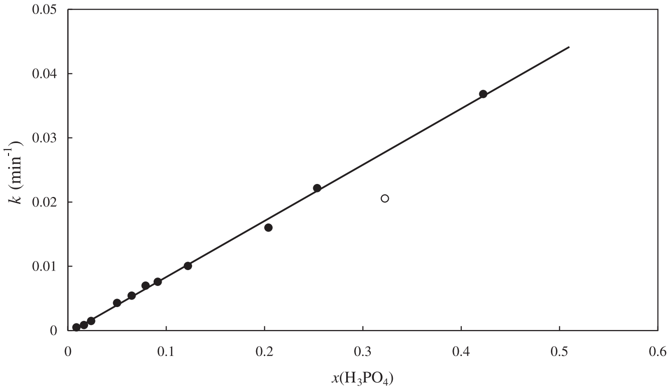
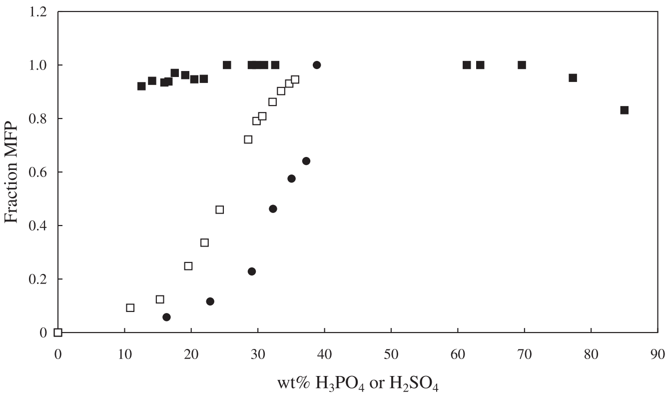


Fig. 4. Equilibrium fraction (α) of monofluorophosphate in H_3PO_4 – H_2SO_4 – H_2O mixtures. □: 15% H_2O, plotted vs. % H_2SO_4; ●: 50% H_2SO_4, plotted vs. % H_3PO_4; ■: ~ 43% H_3PO_4, plotted vs. % H_2SO_4 (see text for information on this series).



in the figure at $x(H_3PO_4) \approx 0.51$, one was obtained using NaF as the initial reactant, the other using Na_2MFP. The origin of the smooth line through the data will be discussed later. Figure 3 shows the apparent first-order rate constants for the kinetics of formation of MFP as a function of $x(H_3PO_4)$. Quite remarkably, the values obtained were linear with $R^2 = 0.997$.[4]

For the phosphoric acid – sulfuric acid – water mixtures, it is more difficult to survey adequately the solvent composition range. In addition to the H_3PO_4 – H_2O binary mixtures (i.e., the 0% H_2SO_4 isopleth), measurements were also made along the following ternary diagram isopleths: ~43% phosphoric acid, 15% H_2O, and 50% H_2SO_4. The results are shown in Fig. 4. In the ~ 43% H_3PO_4 series, the weight composition varied slightly (from 42.3 to 45.5), which accounts for the slightly scattered results. It is remarkable that sulfuric acid has such a large effect on MFP formation. For example, a H_3PO_4–H_2SO_4 – H_2O (42:38:20) mixture yields 100% MFP, whereas a H_3PO_4 – H_2O (42:58) mixture yields only 10% MFP. The results are even more dramatic in the low-water (15%) mixtures where a H_3PO_4 – H_2SO_4 – H_2O (20:60:15) mixture yields 100% MFP, whereas in a 20% H_3PO_4 solution in the absence of H_2SO_4, the yield is ~ 1%. The kinetics in the sulfuric acid solution were typically too fast to measure by our relatively slow NMR method.

Discussion

Formation of MFP in H_3PO_4 – H_2O mixtures

Theory

For the reaction of HF to give MFP, we can write

$$[3] \qquad H_3PO_4 + HF \rightleftharpoons H_2PO_3F + H_2O$$

In terms of the reaction conditions of interest here, both phosphoric acid and water are the predominant species (the solvent), whereas HF and MFP are considered solutes. We have written both of the reactants in their protonated forms because phosphoric acid is a weak acid in water and HF is even weaker. We have no reliable knowledge about the ionization state of MFP. Certainly, it is a stronger acid (in water) than phosphoric acid. However, in the strongly acidic solvents of interest here, we will assume that it is also protonated.

In general, an equilibrium constant is only a "constant" in any given solvent or solvent mixture. For example, in mixtures of ethanol–water, weak acids become considerably weaker as the alcohol content of the solvent increases. One approach to this problem is to define our equilibrium constant K(P–W) for reaction [3] in solvent mixture P–W as

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[4] Most texts on error analysis give a definition for R, see for example ref. 9.

$$[4]\qquad K(P-W) = \left[\frac{c(H_2PO_3F)}{c(HF)}\,\frac{\gamma(H_2PO_3F)}{\gamma(HF)}\,\frac{x(H_2O)}{x(H_3PO_4)}\right] = \left[\frac{\alpha}{1-\alpha}\,\frac{\gamma(H_2PO_3F)}{\gamma(HF)}\,\frac{x(H_2O)}{x(H_3PO_4)}\right]$$

where the γ terms are the conventional concentration-dependent activity coefficients, which can be ignored, providing the concentrations are low enough. This equilibrium constant changes when the solvent composition is changed because the standard chemical potentials of the reactants and products are solvent-dependent. This is often referred to as the "primary medium effect". One approach to this problem is to use "free energies of transfer". Thus, we can write, for the thermodynamic cycle involving reaction [3] in two different solvents, W and P–W

$$[5]\qquad \begin{tikzcd}
H_3PO_4(W) & + & HF(W) & \overset{\Delta_{rxn}G^{o}(W)}{\rightleftharpoons} & H_2PO_3F(W) \arrow[d, "\Delta_t G^{o}(P-W \leftarrow W)"] & + & H_2O(W) \arrow[d, "\Delta_t G^{o}(P-W \leftarrow W)"] \\
H_3PO_4(P-W) \arrow[u, "\Delta_t G^{o}(W \leftarrow P-W)"] & + & HF(P-W) \arrow[u, "\Delta_t G^{o}(W \leftarrow P-W)"] & \overset{\Delta_{rxn}G^{o}(W-P)}{\rightleftharpoons} & H_2PO_3F(P-W) & + & H_2O(P-W)
\end{tikzcd}$$

where $\Delta_t G^{o}(P\text{–}W \leftarrow W)$ are called the free energies of transfer of the species from solvent W (in this case, water) to the solvent mixture P–W. Straightforward analysis of the thermodynamic cycle allows us to write the standard free energy of reaction in solvent mixture P–W as

$$[6]\qquad \Delta_{rxn}G^{o}(P-W) = \Delta_{rxn}G^{o}(W) + \sum_{\text{products}} \Delta_t G^{o}(P-W \leftarrow W) - \sum_{\text{reactants}} \Delta_t G^{o}(P-W \leftarrow W) = -RT\ln K(P-W)$$

The great utility of this equation is that, in principle, the various free energy of transfer terms can be obtained for individual species by thermodynamic measurements such as vapor pressure or solubility. Thus, we can obtain the solvent-composition dependence of the equilibrium constant.

For the reaction of interest, it is not obvious how one would measure the free energy of transfer of HF from H_2O to H_3PO_4. Even if one could find a suitable experimental technique, HF reacts too rapidly in phosphoric acid. It is also not immediately obvious how one would measure this quantity for H_2PO_3F. However, for the purposes of this analysis, we wish to explore the crucial role of the free energy of transfer terms for the two-solvent components, i.e., H_2O and H_3PO_4. The free energy of transfer of species W from W to solvent mixture P–W can be written more formally as

$$[7]\qquad \Delta_t G^{o}[W(P-W) \leftarrow W(W)] = [\mu(W) - RT\ln x_w]_{P-W} - [\mu(W) - RT\ln(x_w = 1)]_W$$

The usual definition for activity coefficients in binary solvent mixtures is

$$[8]\qquad \mu(W) = \mu^{o}(W) + RT\ln x_w + RT\ln \gamma_w$$

with $\ln \gamma_w \to 1$, as $x_w \to 1$; thus, eq. [7] becomes (as we might expect)

$$[9]\qquad \Delta_t G^{o}[W(P-W) \leftarrow W(W)] = RT\ln \gamma_w$$

Applying a similar approach to eqs. [7] and [8] to the transfer of species P from W to a P–W mixture, we obtain

$$[10]\qquad \Delta_t G^{o}[P(P-W) \leftarrow P(W)] = [\mu(P) - RT\ln x_p]_{P-W} - [\mu(P) - RT\ln(x_p = 0)]_W$$

This equation yields

$$[11]\qquad \Delta_t G^{o}[P(P-W) \leftarrow P(W)] = RT\ln \gamma_P - RT\ln \gamma_P(0)$$

where $\gamma_P(0)$ is the limiting activity coefficient of P in pure W.

Solvent-activity coefficients are frequently expressed in terms of an equation of the form (10)

$$[12]\qquad \ln \gamma_w = A{x_p}^2$$

and

$$[13]\qquad \ln \gamma_P = A(1 - x_P)^2$$

By combining eqs. [9], [11], [12], and [13], we readily obtain

$$[14]\qquad \Delta_t G^{o}[W(P-W) \leftarrow W(W)] - \Delta_t G^{o}[P(P-W) \leftarrow P(W)] = 2RT\,Ax_P$$

Combining eqs. [6] and [14] (ignoring contributions from free energy of transfer of the two solutes) we obtain

$$[15]\qquad \ln K(P-W) = \ln K(W) - 2Ax_P$$

predicting a linear dependence of ln K with phosphoric acid mole fraction.

Comparison with experiment

The values of K(P–W), obtained from the data in Fig. 2 using eq. [4], vary from 0.28 to 4.5 over the solvent composition range $x(H_3PO_4) = 0.049$–0.51. A plot of ln(K) vs. $x(H_3PO_4)$ is predicted to be linear by eq. [15]. To see how well the values for α obey this prediction, they were fitted by a non-linear least-squares approach, using Microsoft® Excel Solver, to eq. [4] with the γ terms set to unity and with ln(K) as a linear function of $x(H_3PO_4)$. Thus, the two fitting parameters were the slope and intercept. Figure 2 shows a comparison between observed and calculated values of α. The large variation of K with solvent composition is the cause of the sigmoid shape of Fig. 2. The values obtained for ln K(W) and $2A$ in eq. [15] were –2.7 and –8.5, respectively. No attempt was made to assess the uncertainties in these parameters because the data were obtained over a narrow range of x_p.

The activity coefficients of both W and P in phosphoric acid mixtures can be obtained from vapor-pressure measurements. The calculation is straightforward because, for this system, the vapor contains no phosphoric acid. The 20 °C vapour-pressure data (11) after conversion to water activity coefficients were fitted to eq. [12] to obtain a value of –10.7 for $2A$.[5]

Thus, we conclude that the majority of the large increase in equilibrium constant for the formation of MFP, going from pure water to pure phosphoric acid, is due to the extreme thermodynamic non-ideality of the mixture. In particular, the reaction is strongly promoted by the low water activities, which manifest themselves in the negative value for A in eqs. [12] to [15]. However, the previously mentioned analysis has not included free energy of transfer terms for the two solutes. We also caution that experimental measurements on which the previously mentioned analysis was performed are not of the highest precision.

Formation of MFP in $H_3PO_4 – H_2SO_4 – H_2O$

To obtain an analytical and graphical representation of the variation of α with solvent composition for the H_3PO_4 – H_2SO_4 – H_2O mixtures, the experimental values for α were fitted using a non-linear least-squares approach to equations of the form:

$$[16] \quad K_{\text{app}} = \frac{\alpha}{1-\alpha}\frac{x(H_2O)}{x(H_3PO_4)}$$

with

$$[17] \quad \ln K_{\text{app}} = P_1 w_P(1 + S_{11}w_S + S_{12}w_S^2) + P_2 w_P^2(1 + S_{21}w_S + S_{22}w_S^2)$$

and with w_P and w_S being the wt% of phosphoric and sulphuric acids in the ternary solvent mixture, respectively. The optimal values for the fitting parameters are shown in Table 1.

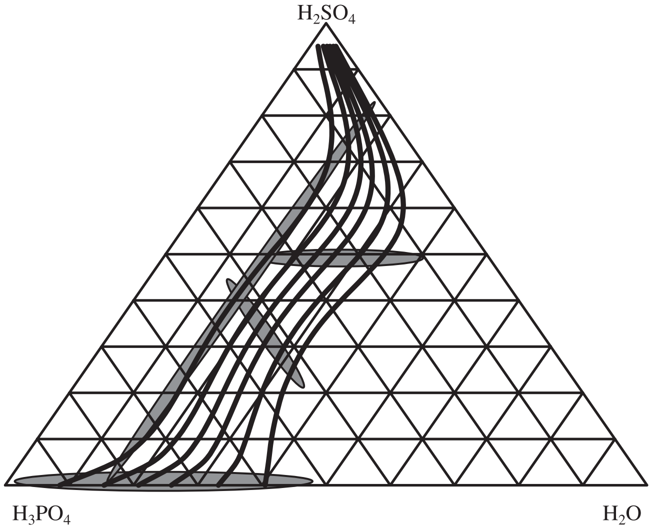
There is no particular theoretical reason for choosing the previously mentioned equations, which are simply convenient representations of the data. With the addition of extra terms, slightly improved fits can be obtained. Figure 5 shows the triangular contour plot from the fit. Whilst the accuracy of the fit may be doubtful in the solvent region that is low in both H_2O and H_3PO_4 (i.e., the H_2SO_4 apex), the form of the graph is unmistakable. Formation of MFP is determined most strongly by the water content of the solution: the lower the water content, the larger the formation of MFP. Quite remarkably, this is a much stronger determinant than the phosphoric acid content of the solution. Thus, we conclude that, as in the case of the binary solvent mixture H_3PO_4 – H_2O, the reaction is being driven by the strong ability of sulphuric acid to depress the thermodynamic activity of water. From the water-activity data for the simple binary mixture H_2SO_4 – H_2O (12), we obtain a value of –24.3 for $2A$.[6] This is, of course, simply a manifestation of the strong dehydrating ability of this acid. This effect is used to advantage in many chemical processes such as the production of concentrated nitric acid (13). HNO_3 – H_2O mixtures form an azeotrope, and thus the acid cannot be concentrated by simple distillation. It is concentrated by extractive distillation using concentrated sulphuric acid. It is interesting to note that phosphoric acid has also been suggested as an extractive distillation agent to concentrate nitric acid. (14).

Table 1. Fitting parameters for the determination of α in H_3PO_4 – H_2SO_4 – H_2O mixtures from eqs. [11] and [12].

P_1	-9.298×10^{-2}
P_2	1.298×10^{-3}
S_{11}	1.189×10^{-1}
S_{12}	-2.473×10^{-3}
S_{21}	1.529×10^{-1}
S_{22}	-1.753×10^{-3}

Note: The fit included 65 data points (as shown in Figs. 2 and 4). The standard deviation between observed and calculated points is 0.04.

Fig. 5. A triangular graph that shows contour plot of the fraction α of MFP formed in H_3PO_4 – H_2SO_4 – H_2O mixtures (see text for details). Moving from left to right across the figure, the contours represent fractions of 0.95, 0.8, 0.6, 0,4, 0.2, and 0.1. The ellipses represent the composition regions where the measurements were taken.



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[5] Vapor-pressure data are probably not extensive enough to justify including higher-fitting terms to this equation. Including these terms does not make a significant difference to the results given here.

[6] To get a good fit, it is necessary to take into account that for the first deprotonation step, sulfuric acid is strong; thus, we define the mole fraction of water as $x_w = n_w/(n_w + 2n_s)$ where n is the number of moles of i, and i is water or sulfuric acid.

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