Variation of Phosphoric Acid Diffusion Coefficient With Concentration

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Phosphoric acid is a weak electrolyte that sometimes shows a complex behavior. This complexity combined with its industrial importance has necessitated an intensive research into its physical and chemical properties.

Solvent extraction processes for purifying wet process phosphoric acid have been widely studied and applied in industrial practice (Ruiz et al., 1985a, 1986, 1988; Marcilla et al., 1989, 1993b). Wider knowledge about the variation of the diffusion coefficient with concentration was necessary in order to gain further experience in a pilot-plant scale extraction column. Several techniques can be used (Ruiz et al., 1985b). In the case of electrolyte solutions, the conductimetric method is very precise. Optical methods have more general application, holographic interferometry being one of the most recent and precise optical methods. We have used this technique to study diffusion, both in liquid and in gel systems (Ruiz et al., 1985c, 1989; Fernández et al., 1986). We have therefore used this technique to determine diffusion coefficients of aqueous solutions of phosphoric acid at 25°C, in the range of concentrations between 5 and 80% in weight.

The results obtained, as well as the results reported by Edwards and Huffman (1959) and by Leaist (1984), show a peculiar shape of the curve diffusion coefficient vs. concentration. An explanation for this shape appears in literature (Edwards and Huffman, 1959; Leaist, 1984), but it only explains the very dilute solution region. In this article we have tried to explain the shape of the curve in the complete range of concentrations.

Experimental

Analysis-grade phosphoric acid 85% (PROBUS) was used without further purification. Solutions were prepared by weighing and the concentration was determined by titration against standardized NaOH using a pH-meter (Crison MicropH 2001).

Diffusion coefficients at 25°C were measured by holographic interferometry. The optical system is the same as that used by Ruiz et al. (1989). The filling procedure has been described in previous articles (Ruiz et al., 1985c; Fernández et al., 1986). For the more viscous solutions the filling procedure was different: first, the denser solution was introduced with a pipette and then, very carefully, the lighter solution was added with a capillary tube over the denser solution trying to keep the diffusion front unaffected. The mathematical treatment to obtain diffusion coefficients from the interference fringes is the same as that described by Ruiz et al. (1985c).

Results

The mathematical treatment assumes the diffusion coefficient varies with concentration in a linear way, so the concentration of the two solutions placed in the diffusion cell must be in the range of linearity. The phosphoric acid solutions used and the diffusion coefficient values obtained are reported in Table 1. Each diffusion coefficient is an average of values calculated from eight to ten interferograms. For each interferogram a mean value is calculated from four to eight values of the diffusion coefficient obtained for each pair of fringes. Figure 1 is a plot of the diffusion coefficient against concentration.

Discussion

The experimental diffusion coefficient of the phosphoric acid shows an unusual variation with the concentration. It remains almost constant in the range of concentrations between

Table 1. Experimental Values of Phosphoric Acid Diffusion Coefficient at 25°C

$c \times 10^3$ (mol/L)	$\Delta c \times 10^3$ (mol/L)	$D_{\text{obsd}} \times 10^9$ (m^2/s)	$S \times 10^9$ (m^2/s)
0.52	0.16	0.882	0.009
1.07	0.11	0.870	0.014
2.27	0.13	0.869	0.009
2.92	0.13	0.869	0.010
5.11	0.16	0.837	0.009
6.80	0.18	0.785	0.008
8.71	0.40	0.675	0.005
13.29	0.39	0.344	0.010

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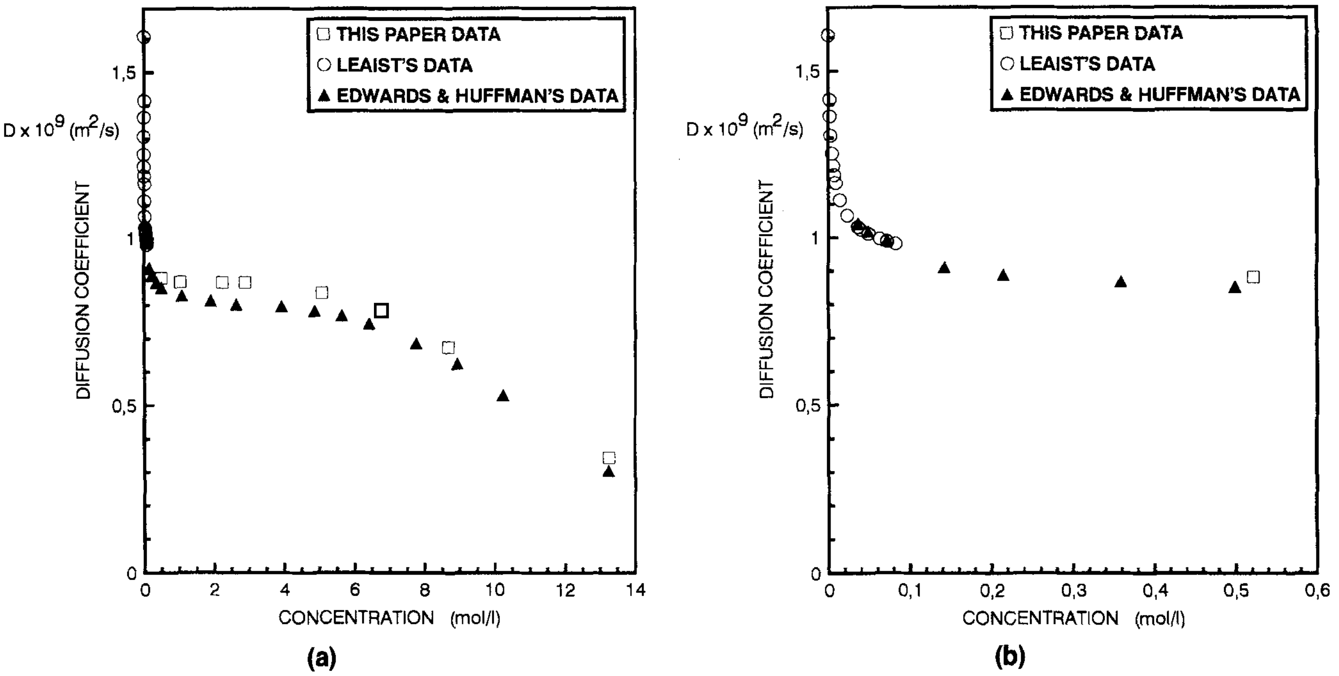


Figure 1. Diffusion coefficients for aqueous solutions of phosphoric acid at 25°C.

(a) Range of concentrations between 0 and 14 mol/L; (b) region of very dilute concentrations.

0.5 and 5 mol/L. For concentrations higher than 5 mol/L, the diffusion coefficient decreases appreciably (Figure 1).

In a previous article, Edwards and Huffman (1959) obtained the diffusion coefficient of aqueous solutions of phosphoric acid using a two-lens Gouy diffusiometer over the concentration range 0.036 to 16 mol/L. Their results are also plotted in Figure 1, the shape of the plot being similar to that obtained in this work. However, Edward and Huffman's results are 10% lower than our results. They also reported an increase in the diffusion coefficient for dilute aqueous solutions. This increase was experimentally confirmed by Leaist (1984) using a conductimetric technique over the concentration range from 0.0012 to 0.083 mol/L. All these experimental results are plotted in Figure 1. Three different stages can be observed: (1) at dilute concentrations the diffusion coefficient decreases quickly with the concentration; (2) in the second step, which is nearly horizontal, the diffusion coefficient varies slightly; (3) the third and final step shows a marked decrease in the diffusion coefficient as the concentration increases.

This unusual behavior has not been sufficiently explained in the three steps. The step corresponding to very dilute concentrations is fully explained by Leaist (1984), using the same arguments as in his article (Leaist and Lyons, 1984) about the diffusion coefficient in dilute aqueous acetic acid solutions. Weak electrolytes diffuse in solution as molecular species together with ions produced by dissociation and the diffusion coefficient can be predicted from the mobilities of the diffusing species.

For the diffusion coefficient of solutions of 1:1 weak electrolyte (for example, acetic acid) Leaist and Lyons (1984) use the expression:

$$\mathfrak{D}=\frac{2(1-\alpha)D_m^o+\alpha(D_\pm^o+\Delta_1+\Delta_2)}{2-\alpha}\left(1+\alpha\frac{d\ln y_\pm}{d\ln c}\right)\qquad(1)$$

If the limiting ionic conductivities are known, $D_\pm^o$ can be calculated from the Nernst equation:

$$D_\pm^o=\frac{2RT}{F^2}\frac{\lambda_+^o\lambda_-^o}{\lambda_+^o+\lambda_-^o}\qquad(2)$$

For dilute aqueous solutions of phosphoric acid, Leaist (1984) assumes that five species exist: $1=H^+$, $2=H_2PO_4^-$, $3=H_3PO_4$, small amounts of the dimer $5=H_6P_2O_8$ and its dissociation product $4=H_5P_2O_8^-$ and extends Eq. 1 to this system with more ionic species.

In terms of the degree of dissociation of H_3PO_4, $\alpha=[H^+]/c$, and the extent of formation of $H_5P_2O_8^-$, $\beta=[H_5P_2O_8^-]/c$, the diffusion coefficient is given by:

$$\mathfrak{D}(c)=\left[(1-\alpha-\beta)D_3^o+\frac{\alpha(\alpha-\beta)D_1^oD_2^o+4\alpha\beta D_1^oD_4^o+(\alpha-\beta)\beta D_2^oD_4^o}{\alpha D_1^o+(\alpha-\beta)D_2^o+\beta D_4^o}+\frac{\alpha(\Delta_1+\Delta_2)}{2}\right]\frac{\eta^o}{\eta}f\qquad(3)$$

where the diffusion coefficient is multiplied by the ratio of viscosities η^o/η and by the thermodynamic factor, f, being $f=(c/RT)(\delta\mu/\delta c)_{T,P}$.

Using for H^+ the value $\lambda_1^o=0.034981\ m^2\Omega^{-1}$ and for $H_2PO_4^-$

the value $\lambda_2^\circ = 0.00330\ \mathrm{m^2\Omega^{-1}}$, Leaist obtained from the Nernst relation a value of $1.60\times10^{-9}\ \mathrm{m^2\cdot s^{-1}}$ for $D_\pm^\circ$. For $H_5P_2O_8^-$ he used the value $\lambda_4^\circ = 0.003\ \mathrm{m^2\Omega^{-1}}$. Using all these values and the experimental values of D_{obsd} in Eq. 3, Leaist obtained at concentrations from 0.01 to 0.0826 mol/L, a value of D_3° essentially constant for the neutral H_3PO_4 molecule ($D_3^\circ = 0.87\times10^{-9}$ m^2/s).

Edwards and Huffman (1959) also fitted their experimental values of phosphoric acid diffusion coefficient by means of a modification of Eq. 1 in order to obtain the value of D_3°:

$$D_m' = \frac{\left[\left(1-\dfrac{\alpha}{2}\right) D_{\mathrm{obsd}}\left(\dfrac{1}{Q}\right) - \dfrac{\alpha}{2} D_i^\circ\right] \Big/ (1-\alpha)}{d\ln a_u / d\ln c} \tag{4}$$

which at zero concentration:

$$\lim_{c\to o} D_m' = D_3^\circ. \tag{5}$$

Edwards and Huffman obtained at infinite dilution the value 0.76×10^{-9} m^2/s which is taken as an approximate value for D_3°. This value is 13% lower than Leaist's result.

It can be observed that Edwards and Huffman used their experimental values of D_{obsd} only for very dilute concentrations (0.07 to 0.5 mol/L) and therefore the complete experimental curve of D_{obsd} against concentration is not explained.

Since the correction factors in Eqs. 1 and 4 can be negligible in the range of concentrations where these equations are used, very similar results would be obtained using a simpler equation:

$$\mathfrak{D} = \frac{2(1-\alpha)D_3^\circ + \alpha D_\pm^\circ}{2-\alpha} \tag{6}$$

This equation shows that $\mathfrak{D}$ (diffusion coefficient at any concentration) depends on two constant parameters, D_3° and $D_\pm^\circ$ (the limiting diffusion coefficients of the molecular and ionized forms of the electrolyte), and on α which is a function of the concentration. Therefore, we can use Eq. 6 to obtain $\mathfrak{D}$ as a function of concentration if we know α as a function of concentration.

In order to check the usefulness of Eq. 6, experimental values from Leaist and Lyons (1984) for dilute aqueous acid acetic solutions, a 1:1 weak electrolyte, were used. Table 2 compares the diffusion coefficients from Leaist and Lyons with those obtained from Eq. 6 using the same parameters, $D_3^\circ = D_m^\circ = 1.20\times10^{-9}$ m^2/s, as Leaist and Lyons (1984). It can be observed that the values are very similar.

Table 2. Acetic Acid Diffusion Coefficients: Leaist and Lyons (1984) vs. Prediction by Eq. 6

$c\times10^3$ (mol/L)	α	$^*D_{\mathrm{obsd}}\times10^9$ (m^2/s)	$^{**}\mathfrak{D}\times10^9$ (m^2/s)
1.76	0.096	1.245	1.238
3.51	0.069	1.227	1.227
5.30	0.057	1.226	1.222
6.15	0.053	1.218	1.221
9.70	0.042	1.215	1.217
20.20	0.030	1.221	1.212
42.80	0.021	1.212	1.208
97.10	0.014	1.200	1.206

*From Leaist and Lyons (1984).

**Calculated from Eq. 6.

Although phosphoric acid is a more complex system and it is not correct to consider it as a 1:1 weak electrolyte, it is possible to describe qualitatively and semiquantitatively the way in which the diffusion coefficient varies with concentration. To do this, the following simplifying hypothesis can be used.

(a) The first step of the curve for dilute solutions (from $c = 0$ to $c = 0.5$ mol/L) can be explained by the dissociation of phosphoric acid, according to the equilibrium:

$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^- \tag{7}$$

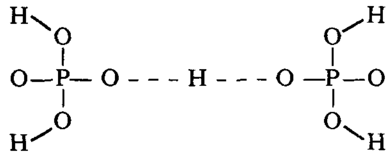
and the equation:

$$k = \frac{\alpha^2 c}{(1-\alpha)} \qquad k = 7.121\times10^{-3}\ \mathrm{mol/L} \tag{8}$$

At infinite dilution, there is complete dissociation and $\mathfrak{D} = D_\pm^\circ = 1.6\times10^{-9}$ m^2/s. In the case of very dilute solutions, until 0.5 mol/L, the diffusion coefficient can be obtained from Eq. 6 using the α values obtained from Eq. 8 and the adequate value of D_3°.

(b) For concentrations between 0.5 and 5 mol/L Eq. 6 can also be used with the α values obtained from Eq. 8. These values are very similar, decreasing slightly as the concentration increases and therefore, the diffusion coefficient obtained from Eq. 6 is nearly constant and that could explain the plateau in the curve diffusion coefficient vs. concentration. However, when the concentration is near 5 mol/L, a more marked decrease in the diffusion coefficient can be observed. This could be due to an association of phosphoric acid molecules, as explained below.

(c) At concentrations higher than 5 mol/L, the interaction of $H_2PO_4^-$ with H_3PO_4 becomes important. According to Pitzer and Silvester (1976), this indicates a tendency towards association to form $H_5P_2O_8^-$. Presumably, this species would be hydrogen bounded as follows:



Evidence for this species has been presented by several authors: Elmore et al. (1965), Selvaratnam and Spiro (1965), Childs (1969, 1970), and Ivakin and Voronova (1973). Presumably, dimerization and even higher degrees of association of the neutral molecules of H_3PO_4 can take place. The rapid increase of phosphoric acid solution viscosity with the concentration can also be a sign of the association. The larger size of the molecular species in solution could explain the decrease of the diffusion coefficient.

In this article, a semiempirical mathematical model based on the ideas explained in points a, b and c is proposed to explain the variation of the diffusion coefficient in a wide range of concentrations. It combines the model proposed in the bibliography for very dilute solutions, with a hypothetical model which takes into account the association of phosphoric acid molecules in the range of 5 mol/L or higher. In order to adapt this model to reality, it would be necessary to know the structure of phosphoric acid at high concentration levels. However, accurate information about the molecular structure of the concentrate phosphoric acid has not been found in literature. The proposed model does not necessarily represent the real structure of phosphoric acid, but it is capable of explaining the way in which the diffusion coefficient varies with concentration.

The simple proposed model assumes that, in a phosphoric acid solution with a certain concentration, the following chemical species are present:

(a) The ionic species $H_2PO_4^-$ and H^+, as well as the molecular species H_3PO_4, in a proportion regulated by Eq. 8.

(b) Phosphoric acid molecules associated by means of hydrogen bonds or other phenomena. This can be represented by the following equilibria:

$$2H_3PO_4 \rightleftharpoons H_6P_2O_8 \quad K_1 = [H_6P_2O_8]/[H_3PO_4]^2 \qquad (9)$$

$$2H_6P_2O_8 \rightleftharpoons H_{12}P_4O_{16} \quad K_2 = [H_{12}P_4O_{16}]/[H_6P_2O_8]^2 \qquad (10)$$

$$2H_{12}P_4O_{16} \rightleftharpoons H_{24}P_8O_{32} \quad K_3 = [H_{24}P_8O_{32}]/[H_{12}P_4O_{16}]^2 \qquad (11)$$

K_1, K_2, and K_3 values must be selected in such a way that for phosphoric acid concentrations lower than 5 mol/L, nearly all the phosphoric acid must be as the species H_3PO_4, whereas for phosphoric concentrations around 5 mol/L, some of the species $H_{24}P_8O_{32}$ must begin to be formed. Its concentration must become rapidly higher as the phosphoric acid concentration increases.

The diffusion coefficient can then be calculated from Eq. 12, which is a modification of Eq. 6 introducing the effect of the molecule association:

$$\mathfrak{D} = [2(1-\alpha)D_3^o(P_M - P_o) + \alpha D_\pm^o]/(2-\alpha) \qquad (12)$$

D_3^o is corrected by means of the difference $(P_M - P_o)$. P_M being the percentage of phosphoric acid (referring to the whole nondissociated phosphoric acid) that is present in the solution in the monomeric form. P_o is the percentage of phosphoric acid (referring to the whole nondissociated phosphoric acid) that is present in the solution in the $H_{24}P_8O_{32}$ form. P_M and P_o are calculated using Eqs. 9, 10, and 11. D_3^o represents the diffusion coefficient of an ideal aqueous solution exclusively formed by the monomeric molecular species H_3PO_4. However, if some of these molecular species are associated and form molecules of greater size, the remaining monomeric species will have greater difficulty of movement in this solution when these large molecules are present. Therefore, a correction of the coefficient D_3^o is suggested: this must be multiplied by the difference between the percentage of phosphoric acid present as remaining monomeric species (P_M) and the percentage of phosphoric acid present as associated molecules (P_o).

Furthermore, Eq. 12, also takes into account the effect of the dissociated species over the diffusion coefficient by means of the coefficient $D_\pm^o$. Thus, if the solution is very diluted, the α value tends to 1 and, therefore, the diffusion coefficient will tend towards 1.6×10^{-9} m²/s, which is the $D_\pm^o$ value calculated from the Nernst law.

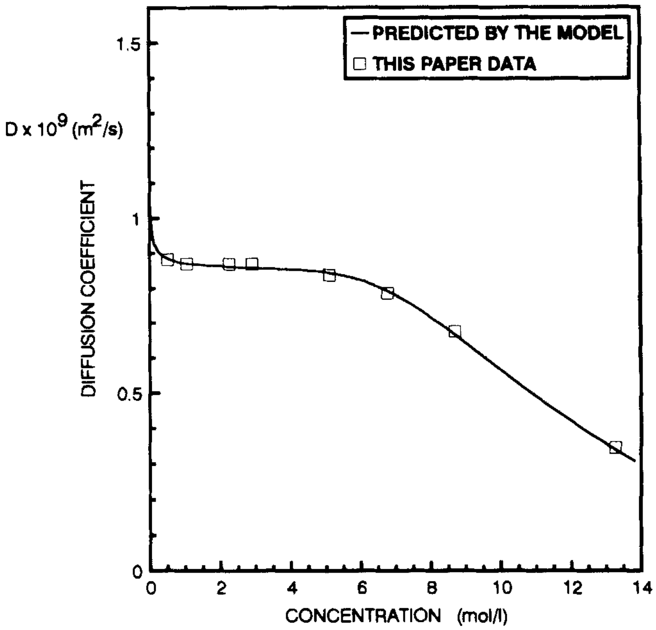


Figure 2. Comparison of diffusion coefficients of phosphoric acid obtained in this article.

Coefficients are predicted using Eq. 12 with the following parameters: $D_\pm^o = 1.6 \times 10^{-9}$, $D_3^o = 0.84 \times 10^{-9}$, $K_1 = 1.1 \times 10^{-6}$, $K_2 = 10^3$ and $K_3 = 8 \times 10^9$.

If this model is applied to the experimental results from this article, a curve as in Figure 2 is obtained which has been calculated solving simultaneously Eqs. 8, 9, 10, 11, and 12 using the following parameters:

$$D_\pm^o = 1.6 \times 10^{-9} \quad D_3^o = 0.84 \times 10^{-9}$$

$$K_1 = 1.1 \times 10^{-6} \quad K_2 = 10^3 \quad K_3 = 8 \times 10^9$$

The D_3^o value is close to Leaist's value (0.87×10^{-9}) and higher than Edwards and Huffman's value (0.76×10^{-9}). The same mathematical model can be used to fit Edwards and Huffman's data. The results are presented in Figure 3 which has been obtained with $D_3^o = 0.78 \times 10^{-9}$. Finally, as Eq. 12 becomes Eq. 6 in the case of very dilute solutions, Eq. 12 could explain Leaist's experimental values (Figure 4). This, however, uses $D_3^o = 0.87 \times 10^{-9}$, which is the same value used by Leaist in his article (Leaist, 1984).

The semiempirical model proposed uses the same parameters (D_3^o and $D_\pm^o$) as proposed by Leaist for very dilute concentrations, as well as the empirical adjusted parameters K_1, K_2, and K_3, introduced to assure the appearance of phosphoric associated molecules when the concentration is 5 mol/L or higher. The model explains the peculiar behavior of the phosphoric acid in a wide range of concentrations.

Acknowledgments

This research was sponsored partially by the C.A.I.C.y T. PA 85-0350 (Ministerio de Educación y Ciencia). Mrs. N. Boluda-Botella was awarded a grant by the Patronato Juan Gil-Albert (Diputación Provincial de Alicante).

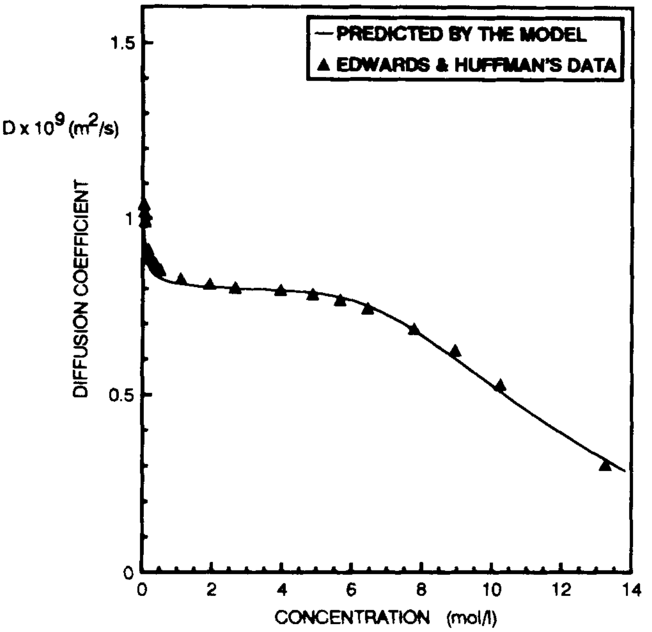


Figure 3. Comparison of diffusion coefficients of phosphoric acid obtained by Edwards and Huffman (1959).

Coefficients are predicted using Eq. 12 with the following parameters: $D^o_\pm = 1.6\times10^{-9}$, $D^o_3 = 0.78\times10^{-9}$, $K_1 = 1.1\times10^{-6}$, $K_2 = 10^3$ and $K_3 = 8\times10^9$.

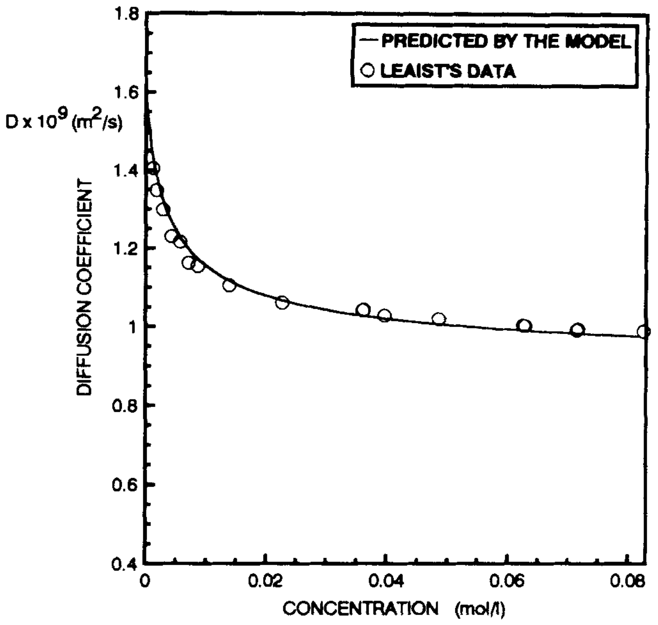


Figure 4. Comparison of diffusion coefficients of phosphoric acid obtained by Leaist (1984).

Coefficients are predicted using Eq. 12 with the following parameters: $D^o_\pm = 1.6\times10^{-9}$, $D^o_3 = 0.87\times10^{-9}$, $K_1 = 1.1\times10^{-6}$, $K_2 = 10^3$ and $K_3 = 8\times10^9$.

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Manuscript received July 28, 1993, and revision received Nov. 1, 1993.