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## Anomalies in the ion transport of phosphoric acid in water and heavy-water environments

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**Abstract.** This paper presents the experimentally determined precise transport data—(tracer) diffusion coefficients in both water and heavy-water environments, together with molar conductivity and viscosity of (ortho)phosphoric acid in water over an extended concentration range at 30 °C. The concentration ( $c$ ) dependence of the diffusion coefficients ( $D$ ), viscosity ( $\eta$ ) and molar conductivity ( $\Lambda$ ) have been analysed. An anomalous depression in the  $D$ – $\sqrt{c}$  curve for both  $\text{H}_3\text{PO}_4$ – $\text{H}_2\text{O}$  and  $\text{H}_3\text{PO}_4$ – $\text{D}_2\text{O}$  systems in the neighbourhood of 0.8 M is observed, which is complementary to the sudden sharp rise observed in the  $\eta$ – $\sqrt{c}$  curve in the neighbourhood of 0.8 M. Although the occurrence of such an anomaly could be inferred from the earlier conductance, e.m.f. and diffusion data, it was never conclusively inferred earlier. This new set of diffusion and viscosity data clearly delineates anomalies in the ion transport of phosphoric acid.

### 1. Introduction

The dynamics of complex liquid systems—especially nondilute aqueous electrolytes—has become a topic of great current interest. The field has been exercised with great ingenuity in the past few years; nevertheless there remains scope for further extension of the data base. A comprehensive and precise set of transport data is of immense significance, firstly, because it can be used as a tool to understand how the dynamical properties of ions or molecules govern the local and global structure of their environment during transport in a complex liquid system, and secondly, they can be used to obtain microdynamic information about the solvent response due to change in solute concentration in complex liquid systems, particularly where the process of charge transfer occurs.

The aqueous solution of phosphoric acid is well known for its inherent complexity due to proton transfer reactions between the three different dissociated states. These proton transfer reactions involving the phosphate radicals play an important part in osteo-sarcoma, tooth decay and other osteogenic diseases. Moreover, this complex liquid has remarkable industrial applications in both biological systems and inorganic compounds. In this paper we report accurate transport data of the aqueous solution of phosphoric acid (henceforth ‘phosphoric acid’ will mean (ortho)phosphoric acid and the anomalies observed therein. The diffusion coefficients of phosphoric acid were measured by the radioactive tracer technique utilizing the sliding cell method [1] over the concentration range from 0.01 to 16.00 M, the molar conductivity over the concentration range from 0.001 to 20.000 M by the standard conductivity bridge and the kinematic viscosity from 0.011 to 6.500 M by a semimicroviscometer.

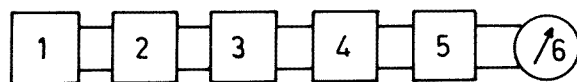
The diffusion coefficients were measured in both water and heavy-water environments. All the measurements were taken at 30 °C.

A brief description of the apparatus together with the solution and tracer is given in section 2. In section 3 we give experimental results, the possible implications of the results, the details of analysis and the inherent limitations of the existing theories when applied to this complex liquid.

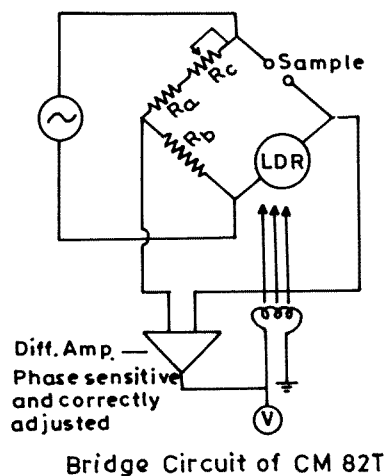
## 2. Experiment

### 2.1. Apparatus

**2.1.1. Diffusion measurements.** The diffusion coefficients have been measured by the radioactive tracer technique utilizing the sliding cell method. In brief, the experimental geometry consists of a diffusion column and a radiation detector, a  $\beta$ -particle spectrometer, vertically placed over the diffusion column. The working formula is based on the Fourier series solution of Fick's second law of diffusion. The details have been given in an earlier work [1], except that the diffusion cells used here are shorter than those previously used. The temperature is kept constant at  $(30.00 \pm 0.05)^\circ\text{C}$ . All precautions are taken to avoid mechanical vibrations.



(1) A.C.Input (2) Bridge of CM 82T (3) Input Buffer  
(4) A.C. Amplifier (5) Detector (6) Indicator



**Figure 1.** A schematic representation of the experimental arrangement for the molar conductivity measurement.

**2.1.2. Conductance measurements.** Conductance measurements were made with a self-balancing conductivity bridge (CM-82T). The conductivity measuring system consists of

an A.C. source (frequency, 1 kHz), a Wheatstone bridge—modified for self-balancing measurements (CM-82T), a conductivity cell and a null indicating device. Such a system is shown in figure 1. The conductivity cells consist of two metal plates of electrodes firmly spaced in a insulating container which serves to isolate a portion of the liquid. This arrangement makes the measured resistance independent of the sample volume. The electrodes are coated with spongy, black platinum which increases the effective surface and reduces the polarization effects. This coating can easily be deposited and is resistant to mechanical and chemical abrasion. Determination of conductivity involves measuring the resistance of a column of solution. To avoid the effect of 'polarization', i.e., the changes in the composition of the measuring cell, alternating current is used. The conductance measurements were made with the cells immersed in a precision oil thermostat, which was maintained at a temperature of  $(30.000 \pm 0.001)^\circ\text{C}$ . The thermostat was set at  $30^\circ\text{C}$  by means of a platinum resistance thermometer in conjunction with a Mueller bridge. Corrections have been made to the measurements for the conductivity of the solvent. The measurements were made at  $30^\circ\text{C}$ .

*2.1.3. Viscosity measurements.* Viscosity (kinetic) was measured with a Cannon manning capillary viscometer (A 735) and evaluated from the viscometer constant ( $k_r$ ) and measured efflux time ( $t$ ) using the relation

$$\eta_{kinetic} = k_r t.$$

Knowing the density ( $\rho$ ) of the particular concentration, absolute viscosity can be evaluated using the relation

$$\eta_{absolute} = \rho \eta_{kinetic}.$$

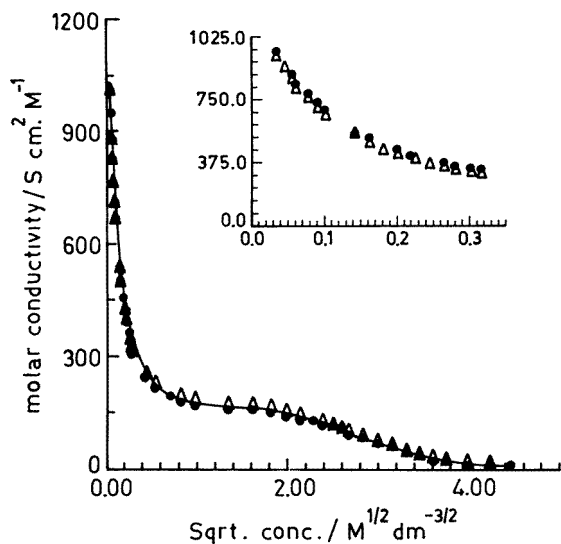
All the measurements were made at  $30^\circ\text{C}$  and the reported data are evaluated from the average efflux time for five consecutive runs.

## 2.2. Tracer

The tracer used for the diffusion measurements is  $^{32}\text{P}$  in a solution of  $\text{H}_3\text{PO}_4$ , obtained from BRIT. The tracer concentration is carefully maintained below  $1.0 \times 10^{-5}$  M so that no error can creep into the measurement, due to the isotope effect [2] and the tracer diffusion coefficient can safely be regarded as the self-diffusion coefficient, assuming that all physical properties of the system (except the radioactive properties) remain constant along the diffusion path.

## 2.3. Preparation of the solution

Conductance water was prepared by redistillation of distilled water and the conductance heavy water was also prepared by the same method with heavy water obtained from BARC. The conductance of these two products is uniformly less than  $1.0 \times 10^{-6}$  S. Crystalline hemihydrate of orthophosphoric acid was dehydrated and recrystallized three times in succession by the method described by Simon and Schulze [3]. Stock solutions of phosphoric acid in both water and heavy water were prepared by dissolving this crystalline acid. Solutions of desired concentrations were then prepared in conductance water by gravimetric dilution of the stock solutions and the concentrations calculated in units of moles per cubic decimetre (M). Carrier free  $\text{H}_3^{32}\text{PO}_4$  was added to stock solution to prepare the radioactive solutions. The specific activity of the stock radioactive solutions was about  $37 \times 10^5$  Bq  $\text{l}^{-1}$ .

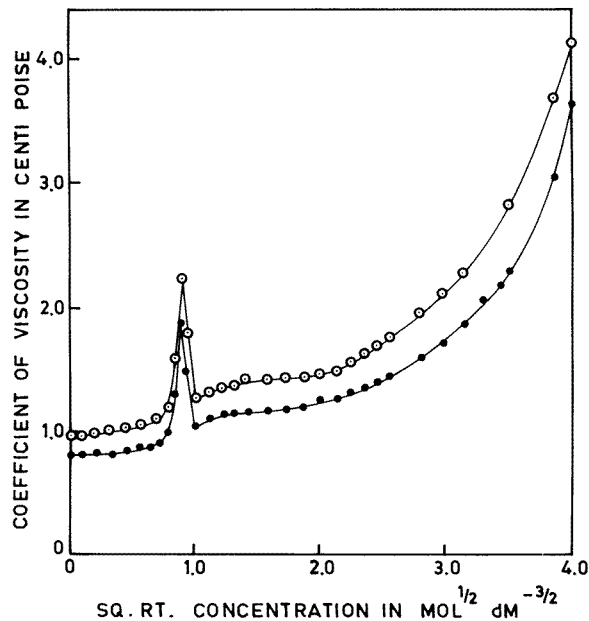


**Figure 2.** The concentration dependence of the molar conductivity of phosphoric acid in H<sub>2</sub>O environment at 30 °C. Inset, data up to 0.1 M concentration on an enlarged scale. ●, data points obtained from the work of Mason and Culvern [4]; Δ, data points obtained from the present work.

### 3. Results and discussion

Figures 2–4 represent our conductivity, viscosity and diffusion data, respectively. All transport data reported in this work are an average of at least three consecutive measurements which are reproducible within a variation of  $\pm 1.02\%$ . The estimated errors, being of the size of the data points, are not shown in the figures. The precision of our measured data (figure 2) of molar conductivity ( $\Lambda$ ) for phosphoric acid in a water environment at 30 °C is about  $\pm 0.113\%$ . Mason and Culvern [4] measured the conductivity of an aqueous solution of phosphoric acid at 25 °C. Figure 2 shows the concentration dependence of both our data and those of Mason and Culvern. Though these two sets of data seem to be on the same curve from figure 2, actually there is an appreciable difference between the two data sets at any particular concentration. In fact these two sets of data give two curves which are almost parallel throughout the whole concentration range. It is not possible to present the parallelism between the two data sets in figure 2 as the  $\Lambda$  scale would have to be enlarged at least by a factor of 100. The concentration dependence of  $\Lambda$  (figure 2) from both the data set shows that  $\Lambda$  falls very sharply (to a value of 104.11 at 0.1 M from 336.05 at 0.001 M in our data set) in the high-dilution region. The  $\Lambda$  versus  $\sqrt{c}$  curve offers a plateau-like region for  $0.10 \text{ M} < c < 4.00 \text{ M}$ . Beyond this region the conductivity decreases monotonically with increasing concentration and approaches the value 1.81 at 20.00 M, but the slope of the  $\Lambda$ – $\sqrt{c}$  curve within the concentration range  $0.001 \text{ M} < c < 0.10 \text{ M}$  is totally different from that in the concentration range  $4.00 \text{ M} < c < 16.00 \text{ M}$ . This finding possibly points to the occurrence of a structural change with increasing concentration.

Figure 3 gives the concentration dependence of the measured viscosity coefficients of phosphoric acid in water and heavy-water environments at 30 °C. The precision of these viscosity data is  $\pm 0.1\%$ . Examination of the viscosity data in figure 3 shows  $\eta$



**Figure 3.** The concentration dependence of the (kinetic) viscosity of phosphoric acid: ●, H<sub>2</sub>O environment; ○, D<sub>2</sub>O environment.

has a monotonic trend of increase with increasing concentration excepting the region where  $1.0 > c > 0.5$ . The sharp rise (having maximum value 1.8601 cP at concentration 0.79 M, within this range) and fall of the viscosity data in both water and heavy-water environments are remarkably complementary to the anomalous depression in the diffusion data in the neighbourhood of 0.8 M. The difference in  $\eta$  in the two different environments at any constant temperature at the same concentration can be explained by considering both the mass effect (a 10% contribution arises due to the difference in masses of the two solvent systems) and the structure effect (a 14–17% contribution arises due to the structural changes in D<sub>2</sub>O and H<sub>2</sub>O).

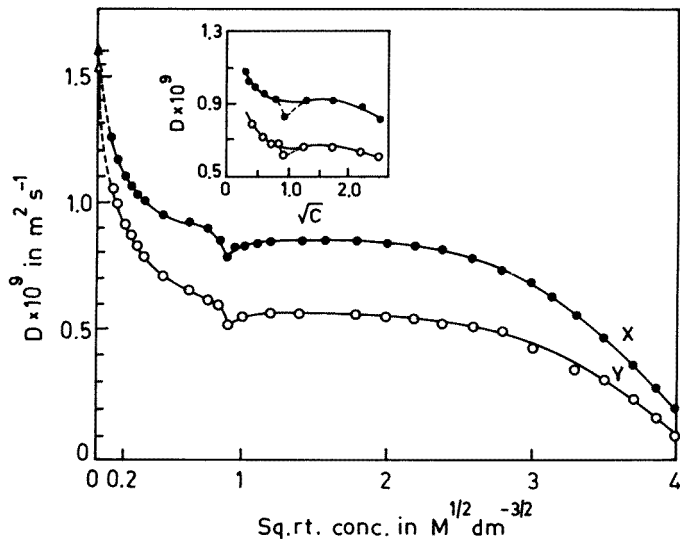
The tracer diffusion coefficients in both water and heavy-water environments at various concentrations at 30°C are measured over the concentration range 0.010 to 16.000 M. The standard deviation in these data varies from 1.0 to 1.7%. The probable error (0.71 times the standard deviation) is less in the lower concentration range. The main source of inaccuracy is the statistical fluctuations in radioactive counting. The precision of the diffusion coefficient ( $D$ ) is about  $\pm 1.02\%$ .

The set of curves in figure 4 shows the variation of the diffusion coefficient,  $D$ , with the square root of concentration,  $c$ , in both water and heavy-water environments. The curves X and Y represent the present set of data. In the inset the data of Das and Changdar [5] are given. It can be seen that the ions diffuse faster in water (X) than in heavy water (Y). Also the diffusion coefficients of phosphate species in the two different environments are only slightly different at very low concentrations but the relative difference becomes larger with increasing concentration and attains a maximum value, and then decreases with the increase of concentration. The difference in  $D$  values at any particular concentration for two systems can be attributed to a combined effect of the difference in mass and structure of the solvents. More explicitly on average a 10% contribution arises due to the mass

difference and the difference in the structure of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  leads to a difference of 14–17%. In the dilute region the contribution due to the mass difference is dominant and in the very concentrated region the structural effect plays the most important role, but the region in between is controlled equally by both of these two effects. The change of  $D$  with  $c$  can be explained by considering the time evolution of the electrostatic interactions among the ions in solution for a particular instant of time, but an exact calculation of all the electrostatic interactions among the ions and the dipoles (water molecules are replaced by suitable dipoles) offers a very complicated integration which is not yet solvable, so we endeavour to pinpoint the characteristics of the curve and pursue the problem with existing semiempirical theories. To compare the rate of diffusion at any particular concentration in two different environments, care was taken to choose the concentrations of  $\text{H}_3\text{PO}_4$ – $\text{D}_2\text{O}$  in units of moles of  $\text{H}_3\text{PO}_4$  per 1105 g of solvent so that the same number of solvent molecules are present in equal concentrations of  $\text{H}_3\text{PO}_4$  in both  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  environments.

Both the curves X and Y in figure 4 show local depressions of  $D$  in the neighbourhood of 0.8 M—precisely at a concentration of 0.807 M for  $\text{H}_2\text{O}$  and 0.804 M for  $\text{D}_2\text{O}$  solvents. Such a dip was observed earlier [6] in the case of the  $\text{H}_3\text{PO}_4$ – $\text{H}_2\text{O}$  system. However, the higher values of the diffusion coefficients in the earlier set of measurements [6] could have resulted from convectional disturbances [7]. In the present measurements care has been taken to avoid such disturbances. In order to check the unexpected low value of the diffusion coefficient near 0.8 M concentration, measurements were made over the concentration range from 0.6–1.0 M in steps of 0.1 M. This confirmed the occurrence of the anomalously low value of the diffusion coefficients near 0.8 M. Such a lowering of the diffusion coefficient at a concentration of 0.84 M has also been reported in the work of Das and Changdar [5] at a temperature of 35 °C in both water and heavy-water environments though they did not investigate the concentration range 0.6–1.0 M so thoroughly and did not make any conclusive inference regarding the anomaly in the diffusion data. According to them the depression was possibly due to the effect of hydration at the particular concentration. This anomalous behaviour can be qualitatively explained by consideration of the degree of dissociation of the phosphoric acid. The degree of dissociation of phosphoric acid as calculated from either the conductance [8] or e.m.f. data [9] passes through a minimum of about 1 M—a phenomenon presumably attributable to an association or hydration reaction of uncertain detail, although several complex species of different dimers and polymers of  $\text{H}_3\text{PO}_4$ ,  $(\text{H}_2\text{PO}_4)^-$ ,  $(\text{HPO}_4)^{2-}$  and  $(\text{PO}_4)^{3-}$  have been suggested [10]. This anomalous decrease of  $D$  can be conjectured as due to the competing contribution of the different dissociated states of the phosphoric acid towards the phosphate diffusion. This complex behaviour cannot be accounted for by continuum theories or by the simple solvation of electrolytes and must take the discrete molecular nature of the solvent and its dynamic interaction with the different states of phosphates into account. Moreover, the effect being very sharp, it may appear that as in some other ionic solutions a liquid–liquid phase separation [11] occurs here, but as our experiments have not provided any evidence in support of such phenomena we need not consider the occurrence of a two-phase region in the phosphoric acid solution. However, the occurrence of the depression in the diffusion curve and the sudden sharp rise in the viscosity curve are complementary to each other and seem to justify the earlier prediction of the existence of minima in the degree of dissociation of phosphoric acid.

Figure 4 also shows some other features, which can be analysed in the course of describing the concentration dependence of the diffusion coefficient over the concentration range from 0.01 to 16.00 M. Any of these  $D$ – $\sqrt{c}$  curves can be divided into three distinct regions—I–III—for convenience of analysis.



**Figure 4.** The concentration dependence of the tracer diffusion coefficient of phosphoric acid: ●, H<sub>2</sub>O as solvent (X) and ○, D<sub>2</sub>O as solvent (Y) (present work); ▲, limiting diffusion coefficient for H<sub>3</sub>PO<sub>4</sub>-H<sub>2</sub>O system from curve (X) and △, limiting diffusion coefficient for H<sub>3</sub>PO<sub>4</sub>-D<sub>2</sub>O system from curve Y; inset, data of Das and Changdar [5].

*Region I.* This extends from infinite dilution to the concentration of 0.15 M. In this range the diffusion coefficient decreases with the increase of concentration. Therefore the diffusion data in this range indicate that the fully hydrated diffusing species (mostly ions in this concentration range) are completely embedded in the sea of water molecules. The average distance between the ions in solution within this concentration range is so large that the hydration as well as the interaction between the hydrated ion and its surrounding solvent molecules remain essentially the same at all concentrations in this region. The only effect of increasing the salt concentration is to increase the interionic attraction due to long-range electrostatic forces. The diffusion potential and electrophoretic effect both being negligibly small in dilute solutions, the decrease in the diffusion coefficient with increasing salt concentrations can be completely attributed to the relaxation effect of the ion atmosphere [12]

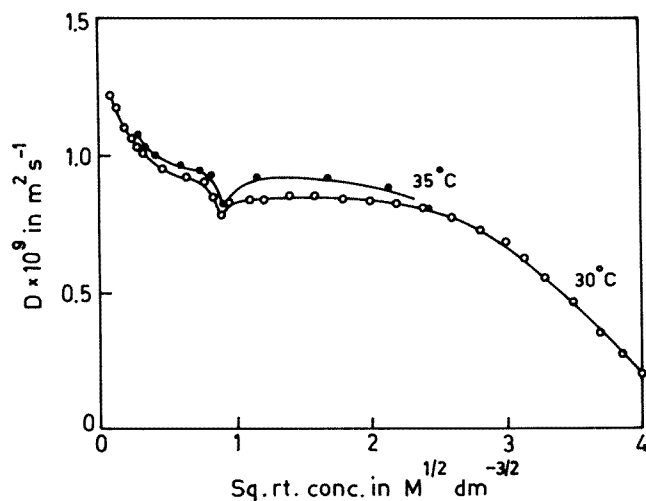
*Region II.* This covers the concentration region from 0.15 to 4.25 M. The  $D-\sqrt{c}$  curve has an almost plateau-like shape in this region. The curves at both 30 °C and 35 °C in figure 5 show that there is no change or very little change in the diffusion coefficient with increasing concentration. This smooth pattern is only perturbed in the neighbourhood of 0.8 M, which has previously been mentioned.

*Region III.* This extends from concentration 4.25 to 16.00 M. The diffusion coefficients in the curves at both 30 °C and 35 °C again start decreasing appreciably with increasing concentration, but the rates are much slower compared to that in region I.

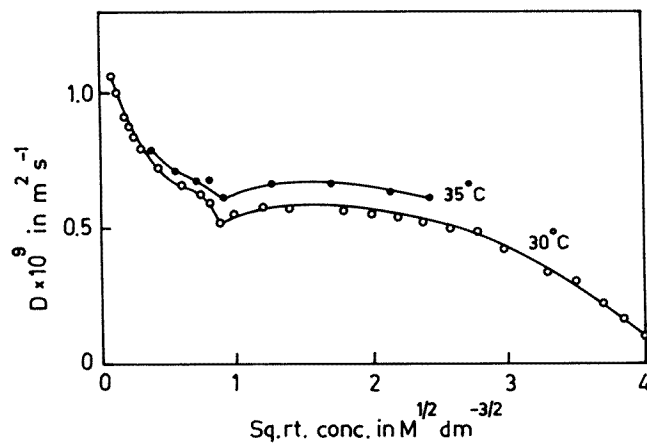
From a comparative study (figures 5 and 6) of the  $D-\sqrt{c}$  data at two different temperatures of the two systems it is readily seen that

- (i) the width of region II shortens with increasing temperature and
- (ii) the position of the dip shifts to higher concentrations with increasing temperature.





**Figure 5.** Tracer diffusion coefficients of phosphoric acid in an  $\text{H}_2\text{O}$  environment at two different temperatures: ●, data from [5]; ○, present work.



**Figure 6.** Tracer diffusion coefficients of phosphoric acid in a  $\text{D}_2\text{O}$  environment at two different temperatures: ●, data from [5]; ○, present work.

Thus it would be interesting to measure the diffusion coefficients over the whole concentration range at temperatures higher than  $35^\circ\text{C}$  and lower than  $30^\circ\text{C}$  for these systems and investigate whether the horizontal part disappears at any temperature.

The different slopes in any of the two curves (figure 4, X or Y) in the regions I and III point to the occurrence of a structural change in the ionic environment which is expected to occur in the concentrated solution of phosphoric acid due to dimerization and polymerization of the different ions present in the solution.

Using the Debye–Hückel–Onsager formula [13] for the concentration dependence of the diffusion coefficient, with the  $\text{H}^+$  and  $(\text{H}_2\text{PO}_4)^-$  equivalent conductivities as  $\lambda_{\text{H}^+} = 346.5 \text{ S cm}^2/\text{equiv.}$  and  $\lambda_{\text{H}_2\text{PO}_4^-} = 31.9 \text{ S cm}^2/\text{equiv.}$ , the Nernst limiting equation was

**Table 1.** Limiting diffusion coefficients. Experimental values were obtained by extrapolating the curves X and Y in figure 4; theoretical values were obtained from Nernst's equation. Each value should be multiplied by  $10^{-9}$  to obtain the absolute value and the units are square metres per second.

System	Experimental value	Theoretical value
H <sub>3</sub> PO <sub>4</sub> -H <sub>2</sub> O	1.60	1.601
H <sub>3</sub> PO <sub>4</sub> -D <sub>2</sub> O	1.52	1.529

found to be

$$D \times 10^5 = 1.601 - 0.124\sqrt{c} \text{ (for the H}_3\text{PO}_4\text{-H}_2\text{O system)}$$

$$D \times 10^5 = 1.529 - 0.121\sqrt{c} \text{ (for the H}_3\text{PO}_4\text{-D}_2\text{O system).}$$

The striking agreement between the extrapolated values of  $D_{\text{H}_3\text{PO}_4\text{-H}_2\text{O}}^0$  and  $D_{\text{H}_3\text{PO}_4\text{-D}_2\text{O}}^0$  (the superscript zero to  $D$  means the diffusion coefficient at infinite dilution) and the theoretically calculated ones (table 1) can be explained in the following way. So far as the dilute solutions are concerned all the H<sub>3</sub>PO<sub>4</sub> readily ionizes and the second and third ionizations are not appreciable. Thus the values extrapolated to zero concentration are for the hypothetical state where the phosphoric acid can be completely dissociated into H<sup>+</sup> and (H<sub>2</sub>PO<sub>4</sub>)<sup>-</sup>, since significant quantities of (HPO<sub>4</sub>)<sup>2-</sup> and (PO<sub>4</sub>)<sup>3-</sup> are not present in this region. As the concentration increases the ionic picture becomes more complicated and this oversimplified picture then needs to be modified. The diffusion data in the plateau region apparently predict that there is no change or little change in the effective ion-ion interaction with the increase of concentration. This is conceivable if it is assumed that some phosphoric acid is carried away by the species H<sub>4</sub>PO<sub>4</sub><sup>+</sup> present in the solution due to the reaction [14]



or



A realization of this phase is afforded in principle by the systems which constitute simultaneously mutual electrostatic repulsion and short-range attractive interaction. A redissociation of the complex cations (H<sub>4</sub>PO<sub>4</sub><sup>+</sup>) is likely to occur in region III, leading to further decrease in the diffusion coefficient. The competition of redissociation and statistical weightage of the contribution to the diffusion rate due to different dissociated species also leads to instabilities of individual species and is governed by the dynamics of their fluctuations. However, the plateau region could be equally attributed to a range of complexing (ion-pairing) phenomena, in which the simplest way is to consider ion pairing as a two-step association process. Because of the high dielectric constant of water it is difficult to distinguish between the relative importance of these two factors.

A thorough qualitative analysis of the transport mechanism, clarifying the 'observed anomalies' in such a complicated system, is yet to be developed. Some commendable works may be performed using the theories of Dodo *et al* [15] or Chhah *et al* [16]. While doing so, proper modifications have to be introduced to take care of the complexity of the system referred to, because both of these two theories deal with simpler systems—binary electrolyte solutions. These transport data can also be rationalized in terms of the ion pair formalism theory of Bjerrum [17]. Bjerrum's approach divides the population of ions around any particular ion into free ions and ions forming ion pairs. To estimate the population of these ion pairs the following assumptions are made.

- (i) The ion pairs act as ideal solutes, i.e. have unit activity coefficients.
- (ii) Free ions are treatable by Debye–Huckel type equations.
- (iii) There is an association equilibrium.

These assumptions can also account for the comparatively rapid decrease of the molar conductivity observed at low concentrations (figure 2) satisfactorily. This treatment needs the specification of a maximum distance of separation to define an ion pair. In Bjerrum's original work the pairs were defined as those for which the distance of separation is less than the distance  $R_B = b/2 = |z_+z_-e^2/2\epsilon kT$ , where  $b$  is the Bjerrum length,  $z_i e$  ( $i = +, -$ ) is the charge on an ion of species  $i$ , and  $\epsilon$  is the dielectric constant of the medium; other symbols have their usual meaning. This successful scheme can be extended to higher concentrations if it is assumed that the degree of association,  $\alpha$ , increases with increasing salt concentration. After a certain concentration the association reaches a steady value, thus showing the plateau region in the  $D-\sqrt{c}$  curve. At concentrations above this region a redissociation of the ion pair occurs resulting in the association asymptotically reaching unity and the diffusion coefficient a very small value.

However, such explanations are not above criticism [18], specially around the concentration of 0.8 M where the presence of a large number of aggregates has to be postulated. The conceptual difficulties of such an approach are well known [19]. The postulation of an apparent redissociation effect is corroborated by various theoretical arguments [20–22]. One comes across conflicting views and complex reasoning while trying to interpret the observed peculiarities. Hence it will be of great interest in modelling the ion distributions that are the typical properties of such systems. Calculation of the pair interaction coefficient will give the most realistic details of the interparticle distributions. These coefficients together with the velocity cross correlation coefficients (which can be calculated by extending the formalism of a ternary system [23] to a pentanary system) will characterize the coupled pairwise diffusion of ions and can be related to the corresponding solvent averaged ion–ion potentials. A calculation of these coefficients over the whole concentration range and comparison with experimental values given for 1:1, 1:2 and 1:3 electrolyte systems [24–26] may help to give a satisfactory description of the structure of these systems in correlation with their environment and to gain much information so that we can explain how the dynamical properties of the diffusing species govern the local and global structure of its environment during transport for a complex liquid system consisting of dissociating electrolyte.

#### 4. Conclusion

The isothermal transport coefficients in the complex liquid systems of  $\text{H}_3\text{PO}_4\text{--H}_2\text{O}$  and  $\text{H}_3\text{PO}_4\text{--D}_2\text{O}$  have been measured over a wide range of concentration. A comparison of the measurements to Debye–Huckel–Onsager theory indicates that the charged species are predominantly  $\text{H}^+$  and  $(\text{H}_2\text{PO}_4)^-$  in the dilute region. Under these conditions the transport coefficients varies almost linearly with concentration.

However the ionic picture becomes complicated in the nondilute region. As the concentration reaches the neighbourhood of 0.8 M, the transport data profile shows the following anomalies: (i) a pronounced depression minimum in the diffusion coefficient profile and (ii) a significant inflation maximum in the viscosity profile. The diffusion minimum in the diffusion coefficient shifts towards higher concentration with increasing temperature. The anomalies in the data—the depression minimum in the diffusion coefficient curve and the inflation maximum in the viscosity curve—are complementary to each other.

The appearance of this anomaly is significant in the context of ion transport in complex liquids. Although the reason for this anomaly is not quite clear it might arise from the competing interaction between the different dissociated states of phosphoric acid.

The transport data in the more concentrated region can be rationalized either from the concept of ion pair formation or from the formation of a complex ion followed by its redissociation at higher concentration. For a complete understanding of the observed phenomena one requires a fully developed theory of ion transport in such complex liquid systems, which is not yet available. An analysis in the purview of Bjerrum's theory or the most recent theories of Dodo *et al* or Chhah *et al* might open new avenues towards the understanding of complex liquid systems.

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