

CHAPTER - V

ULTRASONIC VELOCITY AND ABSORPTION STUDIES IN AQUEOUS ELECTROLYTES

5.1 ULTRASONIC VELOCITY STUDIES:

Ultrasonic velocity and absorption measurements provide information concerning the structure of electrolytic solutions as well as both chemical and physical processes occurring in these solutions.

The study of ultrasonic velocity and adiabatic compressibility in aqueous solutions of electrolytes over a wide range of concentrations and temperature is of paramount importance, as it provides information about the nature of molecular interactions. Extensive work has been carried out by a number of workers [1-3] in this area and the parameters such as adiabatic compressibility, apparent molar compressibility and hydration number have been determined in aqueous solutions of different electrolytes. It is very well recognised that the polar liquids such as water exhibits quasi-crystalline structure due to the short range order existing in these liquids. When an electrolyte is added to such a polar liquid, the ions of the dissociated electrolytes disturb the prevailing short range ordering among the water molecules. This leads to the establishment of a new structure around the ions in which the solvent dipoles are oriented about each ion. This effect becomes

particularly significant in concentrated solutions as a major portion of the solvent molecules become involved in the immediate solvent sheath surrounding each ion of the electrolyte. Such an effect is significant because the electric field of ions exert a considerable electrostrictive effect on the solvent molecules. This leads to the reduction of volume as well as the compressibility of the solvent molecules. This in turn leads to an increase in sound velocity by a significant amount due to the addition of a simple strong electrolyte to water. So in most of the electrolytes, the ultrasonic velocity increases with increasing solute concentrations in a non-linear fashion.

For aqueous solutions of electrolytes like uranyl chloride, uranyl nitrate, strontium iodide and zinc iodide [4], the ultrasonic velocity studies have shown a decrease of sound velocity with increase of concentration of the electrolytes. This is contrary to the general observation that the sound velocities are more than that of water in aqueous electrolytic solutions. However, the decrease in ultrasonic velocity observed in this case can be explained as due to the presence of heavy ions. Heavy ions have smaller velocity of brownian motion. Similar observation of decrease in ultrasonic velocity with increase in concentration of electrolytes have been reported in the case of aqueous solutions of cadmium iodide, cadmium bromide [5] and silver nitrate [6].

The present ultrasonic velocity studies were undertaken in aqueous solutions of ammonium chloride, ammonium oxalate, ammonium di-hydrogen phosphate, sodium di-hydrogen phosphate and potassium di-hydrogen phosphate with a view to understand the nature of solute-solvent interactions in these aqueous electrolytes having common cation and anion over a temperature range of 303 K, 313 K and 323 K. These electrolytes were divided into two groups. Group-I consists of ammonium chloride, ammonium oxalate and ammonium di-hydrogen phosphate which have a common cation NH_4^+ . Whereas group-II consists of sodium di-hydrogen phosphate and potassium di-hydrogen phosphate having a common anion H_2PO_4^- .

Aqueous solutions of ammonium chloride and ammonium di-hydrogen phosphate were prepared by taking known amount of electrolyte in double distilled water so as to obtain concentrations in the range 0.01 mole fraction to 0.08 mole fraction. The concentration range chosen for ammonium oxalate was from 0.001 mole fraction to 0.008 mole fraction. Whereas for sodium di-hydrogen phosphate and potassium di-hydrogen phosphate the concentration range was from 0.001 mole fraction to 0.03 mole fraction. The lower concentration range was chosen for aqueous ammonium oxalate, sodium di-hydrogen phosphate and potassium di-hydrogen phosphate due to their low solubility in water.

Ultrasonic velocity measurements were made at temperatures of 303 K, 313 K and 323 K using pulse echo interferometer at an RF frequency of 10 MHz with a

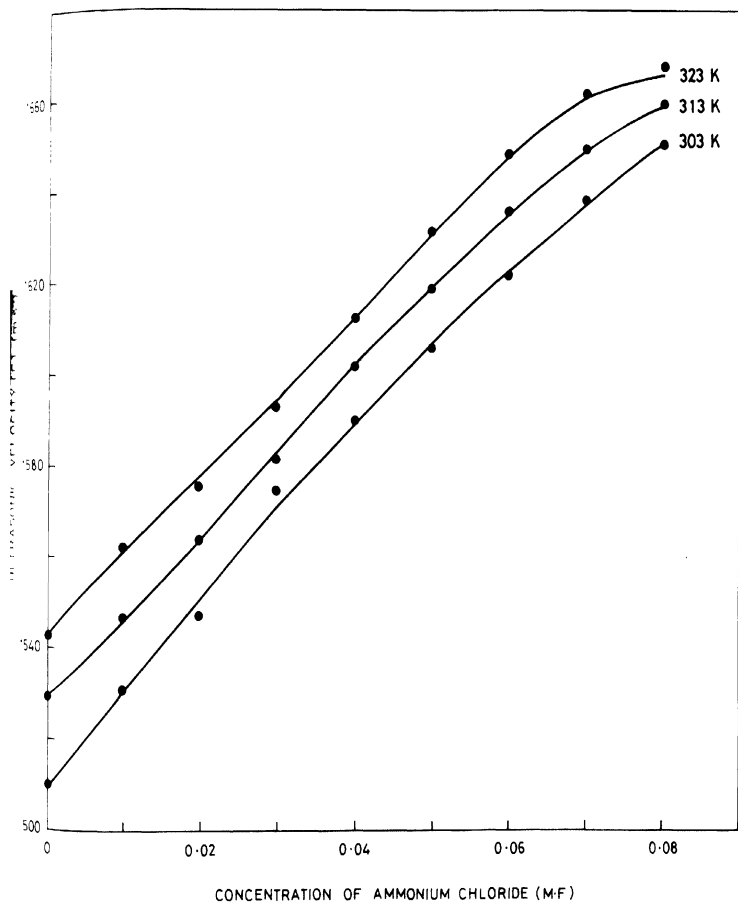


FIG 5-1. ULTRASONIC VELOCITY VS CONCENTRATION OF AMMONIUM CHLORIDE (M.F)

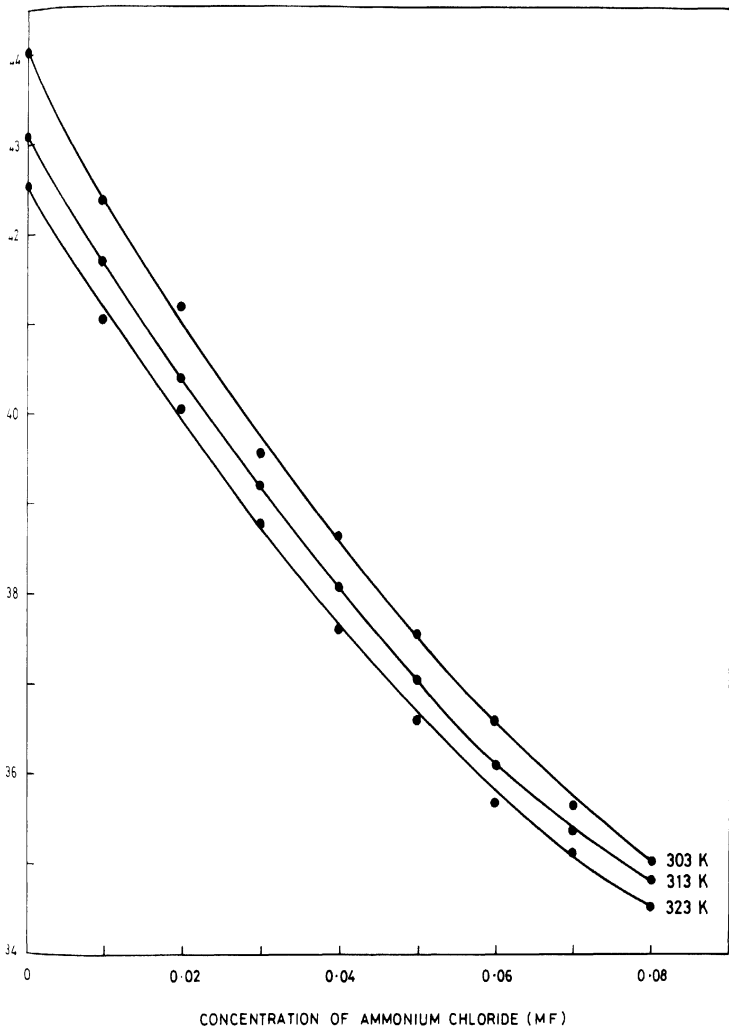


FIG-5.2. ADIABATIC COMPRESSIBILITY VS CONCENTRATION OF AMMONIUM CHLORIDE (M.F)

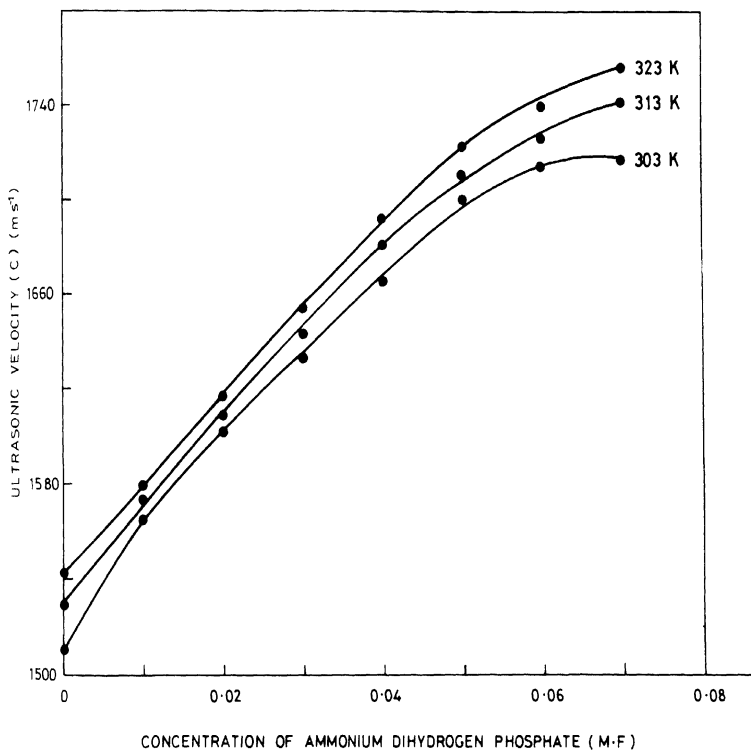


FIG-5.3. ULTRASONIC VELOCITY VS CONCENTRATION OF AMMONIUM DIHYDROGEN PHOSPHATE (M.F)

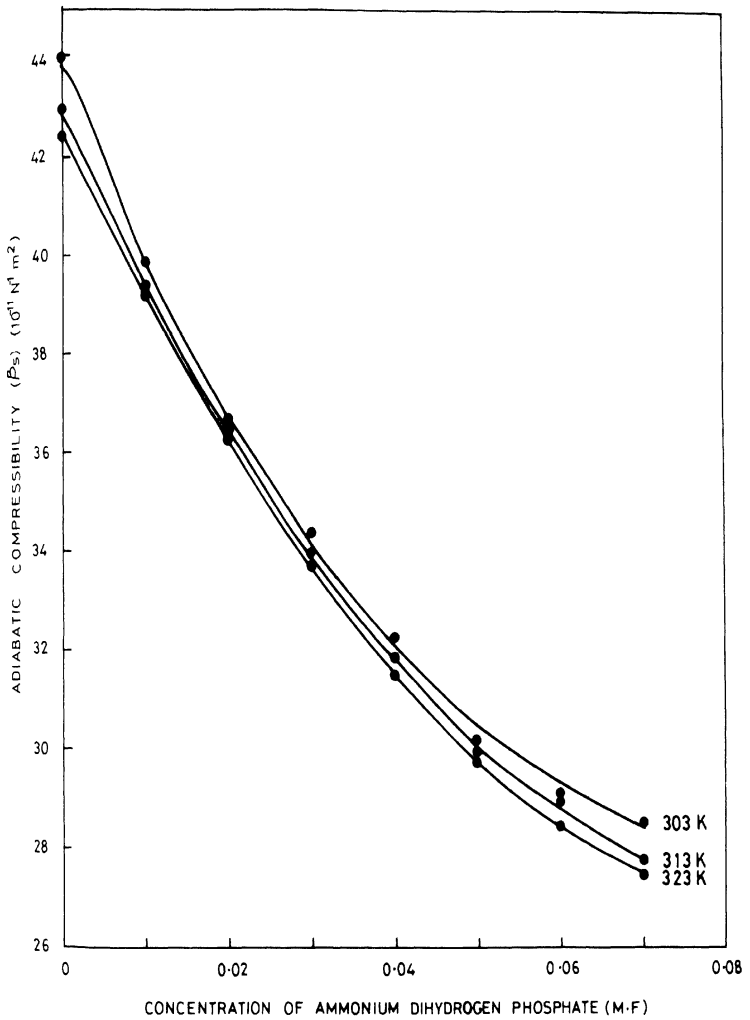


FIG-5.4. ADIABATIC COMPRESSIBILITY VS CONCENTRATION OF AMMONIUM DIHYDROGEN PHOSPHATE (M.F)

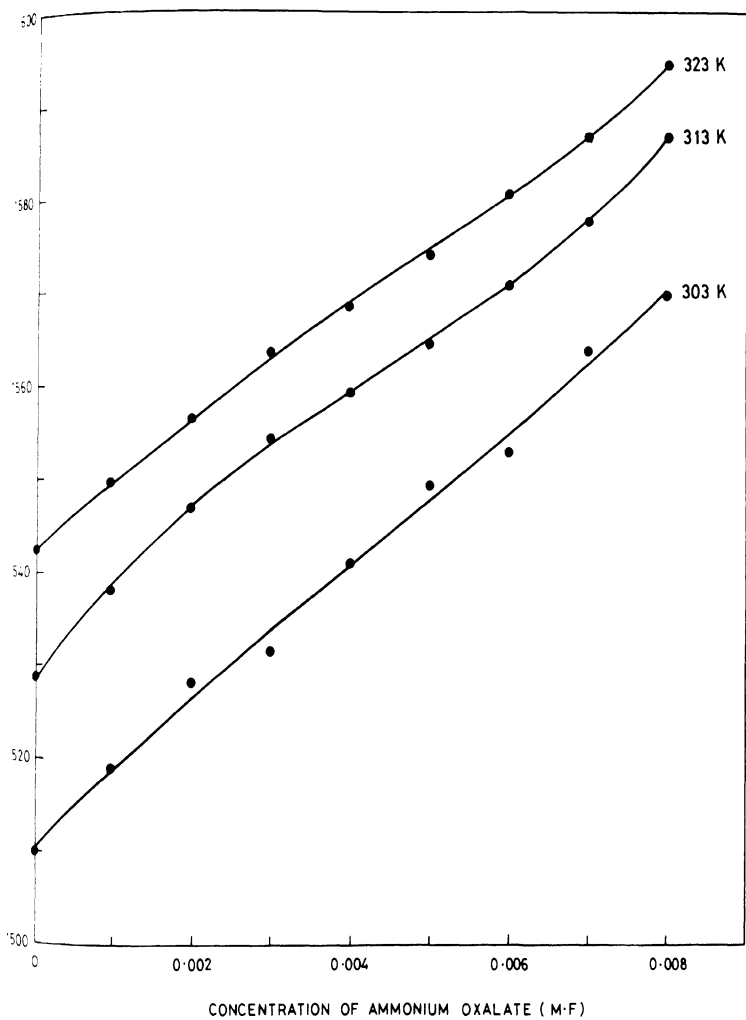


FIG-5.5. ULTRASONIC VELOCITY VS CONCENTRATION OF AMMONIUM OXALATE (M.F)

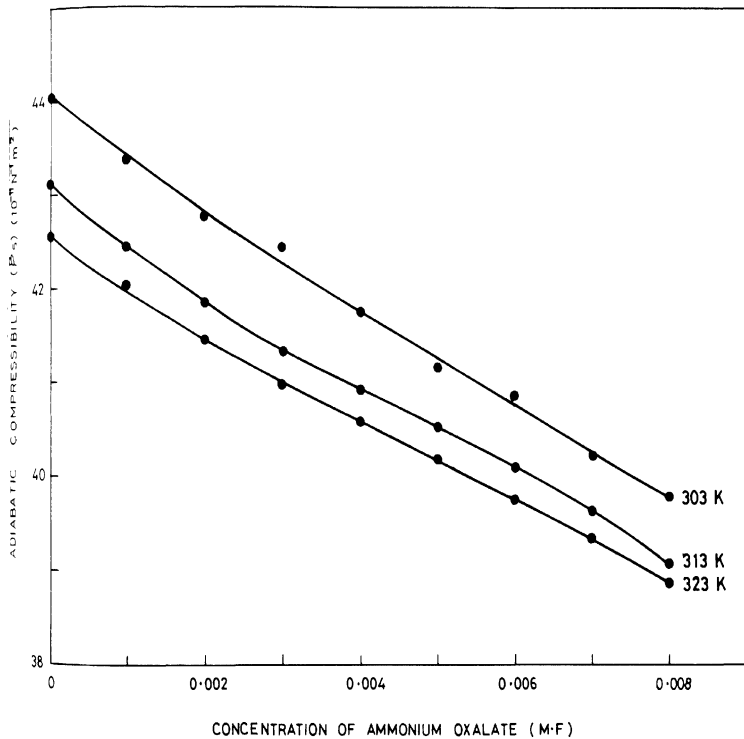


FIG-5-6. ADIABATIC COMPRESSIBILITY VS CONCENTRATION OF AMMONIUM OXALATE (M:F)

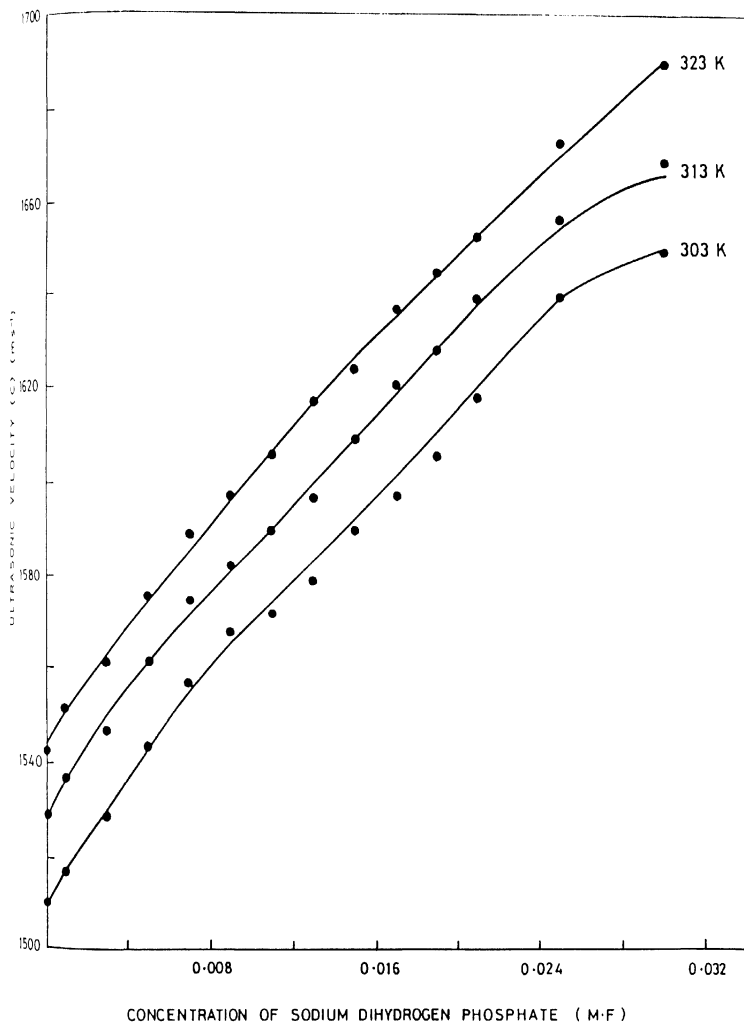


FIG-5-7. ULTRASONIC VELOCITY VS CONCENTRATION OF SODIUM DIHYDROGEN PHOSPHATE (M·F)

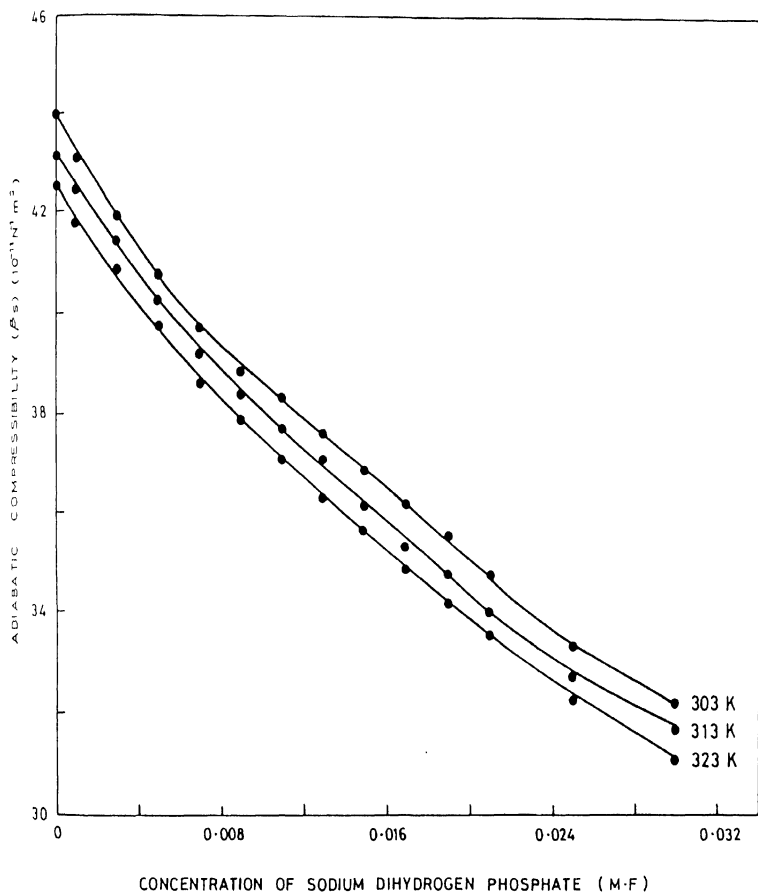


FIG-5.8, ADIABATIC COMPRESSIBILITY VS CONCENTRATION OF SODIUM DIHYDROGEN PHOSPHATE (M.F)

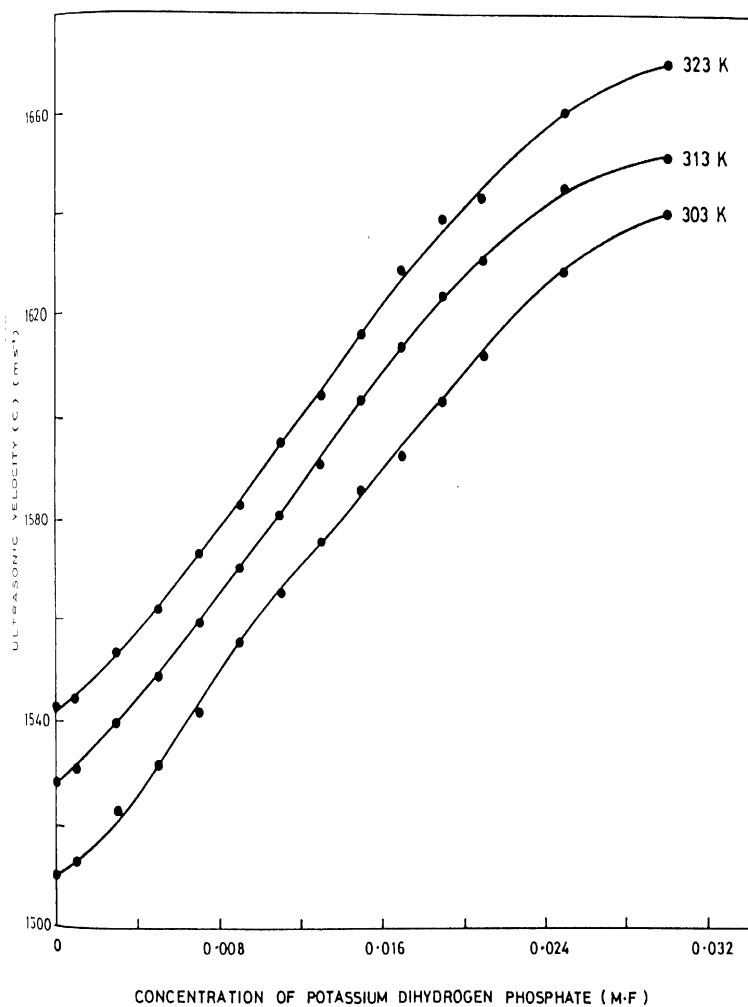


FIG-5-9. ULTRASONIC VELOCITY VS CONCENTRATION OF POTASSIUM DIHYDROGEN PHOSPHATE (M.F)

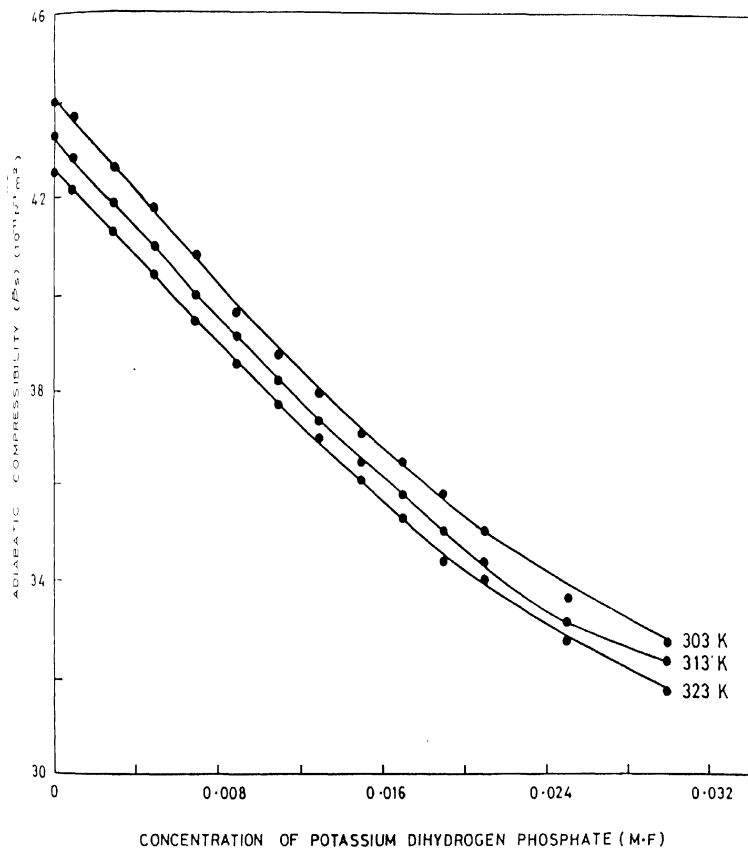


FIG-5-10. ADIABATIC COMPRESSIBILITY VS CONCENTRATION OF POTASSIUM DIHYDROGEN PHOSPHATE (M·F)

specially fabricated cell described in chapter - II. Throughout the experiment the cell was maintained at the required temperature by circulating water from a thermostatically controlled water bath through the double walled cell and the temperature was maintained to an accuracy of $\pm 0.1K$. Using the values of ultrasonic velocity and density, the adiabatic compressibility is calculated and the readings are shown in the tables 5.1 - 5.15. The variation of these parameters with solute concentration is shown graphically in figures 5.1 - 5.10. All the data were fitted to a suitable polynomial for least error in fitting the data. This is achieved using a basic program "POLY" given in the appendix - II.

5.2 RESULTS AND DISCUSSION

It can be seen from the figures 5.1, 5.3, 5.5, 5.7 and 5.9 that the ultrasonic velocities in aqueous solutions of ammonium chloride, ammonium oxalate, ammonium di-hydrogen phosphate, sodium di-hydrogen phosphate and potassium di-hydrogen phosphate increases non-linearly with increase in solute concentration. The ultrasonic velocity is also found to increase with increase of temperature. The variation of adiabatic compressibility with electrolyte concentration (figures 5.2, 5.4, 5.6, 5.8 and 5.10) shows that it decreases non-linearly. The variation of intermolecular free length with increasing solute concentration given in tables 5.1-5.15 shows a similar behaviour as the adiabatic compressibility. The hydration

numbers were also calculated for these aqueous electrolytes. Among the group-I electrolytes, the ammonium oxalate has the largest value of hydration number at 303 K. The hydration number of ammonium di-hydrogen phosphate is larger compared to ammonium chloride for any given concentration. At 303 K, the hydration number varies from 3.86 to 2.36 for ammonium oxalate. Whereas it varies from 3.86 to 2.36 and from 10.58 to 4.67 for ammonium chloride and ammonium di-hydrogen phosphate respectively. Among the group-II electrolytes, the hydration number is larger for sodium di-hydrogen phosphate than potassium di-hydrogen phosphate. For sodium di-hydrogen phosphate, the hydration number varies from 23.24 to 8.6 at 303 K with increasing solute concentration. Whereas for potassium di-hydrogen phosphate it varies from 10.77 to 8.21.

The salient features of these studies are summarised as follows:

1. The ultrasonic velocity in aqueous solutions of ammonium chloride, ammonium oxalate, ammonium di-hydrogen phosphate, sodium di-hydrogen phosphate and potassium di-hydrogen phosphate are found to increase non-linearly with increase of solute concentration.
2. The ultrasonic velocity is found to increase with increase of temperature.
3. The adiabatic compressibility of aqueous ammonium chloride, ammonium oxalate, ammonium di-hydrogen

phosphate, sodium di-hydrogen phosphate and potassium di-hydrogen phosphate solutions decreases with increase of solute concentration.

4. The intermolecular free length for these aqueous electrolytes decreases with increase of electrolyte concentration.
5. Among the group-I electrolytes, the hydration number is largest for ammonium oxalate. It is larger for ammonium di-hydrogen phosphate compared to ammonium chloride at any particular concentration.
6. Among the group-II electrolytes, the hydration number is larger for sodium di-hydrogen phosphate compared to potassium di-hydrogen phosphate at any given concentration.

It is seen from the tables 5.1-5.15 and from the figures 5.1, 5.3, 5.5, 5.7 and 5.9, that the ultrasonic velocities in aqueous solutions of ammonium chloride, ammonium oxalate, ammonium di-hydrogen phosphate, sodium di-hydrogen phosphate and potassium di-hydrogen phosphate are higher than that of water. The ultrasonic velocities seem to increase non-linearly as the concentrations of the electrolytes are increased. The increase in ultrasonic velocity in any solution indicates a greater association of its molecules. The greater association may be brought either by ionic hydration of the solutes [7] or through hydrogen bonding [8,9] between the solute and the solvent

molecules. In the present study, the increase in the ultrasonic velocity in aqueous solutions of ammonium chloride, ammonium oxalate, ammonium di-hydrogen phosphate, sodium di-hydrogen phosphate and potassium di-hydrogen phosphate can be explained by resorting to Flickering cluster model of water [10]. According to this model, the water is supposed to consist of hydrogen bonded clusters and unbonded water molecules. The molecule in the interior of the clusters are quadruply bonded (ice - like) and unbonded water molecules are supposed to occupy the space in between the clusters. The clusters are sometimes referred as 'open structure' water and the dense monomeric fluid is referred to as 'closed structure' water. The mixture is a dynamic mixture and the break down of clusters is a cooperative process. When one hydrogen bond breaks in the cluster, the whole cluster breaks down resulting in an increase in the close packed structure of water.

5.2.1 Ultrasonic velocity studies in Group - I Electrolytes

When the electrolytes ammonium chloride, ammonium oxalate and ammonium di-hydrogen phosphate are dissolved in water, they dissociate and exist in ionic form. The cation NH_4^+ thus produced by dissociation of the electrolytes in water is known to be a water structure breaker [11]. Hence this ammonium ion (NH_4^+) would first disrupt the open structure of water as soon as the electrolytes are dissolved in water. This structure breaking tendency of NH_4^+ ion increases the unbonded close packed structure of water

molecules in the medium, an action which would be followed by the structural reorganisation leaving the molecules in closely fitting helical cavities. Also NH_4^+ ion which has the same size and geometry similar to that of water monomer. Due to this property, depending on circumstances, it can occupy both nodes and voids of water framework [12]. The increase in the high density monomer population of water molecules results in an increased cohesion among the water molecules. This increased cohesion among the water molecules in the medium is responsible for observed increase in the ultrasonic velocity [13].

The ultrasonic velocities in aqueous solutions of ammonium chloride, ammonium oxalate and ammonium di-hydrogen phosphate are found to increase with increase of temperature. This behaviour is similar to that of pure water. As the temperature increases, more and more number of hydrogen bonds in open packed structure of water breaks and more and more monomers are available. These monomers occupy the vacant space and increase the cohesion between the water molecules. A similar explanation may also hold good for the aqueous solutions of ammonium chloride, ammonium oxalate and ammonium di-hydrogen phosphate. In these solutions, the non-linearity between the ultrasonic velocity and the solute concentration may be attributed to the increased cohesion among the water molecules brought about by the addition of ammonium chloride, ammonium oxalate and ammonium di-hydrogen phosphate to water [13]. In addition, it is also probable that the ionic hydration may

also play an important role in bringing about an increased cohesion among the water molecules. This also results in the increase of ultrasonic velocity [7]. The above discussion for the observed increase in the ultrasonic velocity in these aqueous solutions of electrolytes is further supported by the calculated values of hydration number for these systems.

5.2.2 Ultrasonic velocity studies in Group-II Electrolytes

When sodium di-hydrogen phosphate is dissolved in water, it dissociates into Na^+ ion and H_2PO_4^- ion. The Na^+ ion is known to be a water structure maker [11]. This Na^+ ion restricts the overall motional freedom of the water molecules. This leads to an increased cohesion among the water molecules in the medium. The potassium di-hydrogen phosphate dissociates into K^+ ion and H_2PO_4^- ion in an aqueous medium. The K^+ ion which is a water structure breaker [11] would first disrupt the open packed structure of water and thereby release high dense water monomers. The increased population of high density water monomers leads to an increased cohesion among the water molecules. This increased cohesion among the water molecules brought about by the addition of sodium and potassium di-hydrogen phosphates leads to an increase in the ultrasonic velocity in the aqueous solutions electrolytes [13]. The ultrasonic velocity increases with increase of temperature in the aqueous solutions of sodium and potassium di-hydrogen phosphates. This behaviour is similar to that observed in

aqueous solutions of group - I electrolytes. Hence the discussion given for the aqueous solutions of group - I electrolytes also holds good for the aqueous solutions of sodium and potassium di-hydrogen phosphates.

The ultrasonic velocity measured in aqueous solutions of sodium di-hydrogen phosphate is found to be higher than the ultrasonic velocity measured in the aqueous solutions potassium di-hydrogen phosphate at any given concentration. This may be probably explained as follows.

When an electrolyte is added to water, some water molecules get arranged around each ion due to their large dipole moment. This interaction between the ion and the surrounding water molecules is termed as hydration. The first layer of firmly bound and highly incompressible water molecules forms the primary hydration. The water molecules which surround the primary hydrated molecules forms the secondary hydration [14]. The sodium ion because of its high charge density not only polarises, immobilises and electrostricts nearest water molecules, but also induces additional order beyond the first layer. Where as the potassium ion which has a lower charge density compared to sodium ion have a relatively weak electrostrictive fields, so it produces ordering of water molecules only in the first layer. This layer is immediately followed by a structure broken region, where the molecules are more mobile than in pure water. One can thus expect that, the compressibility of the sodium salt solutions to be less than that of the potassium salt solutions of same

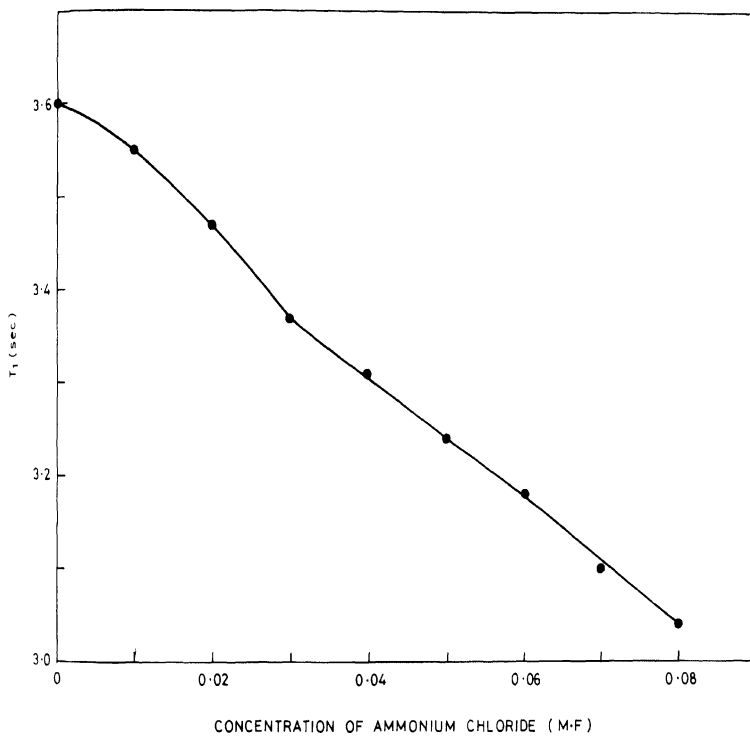


FIG-5-11. RELAXATION TIME (T_1) VS CONCENTRATION OF AMMONIUM CHLORIDE (M·F)

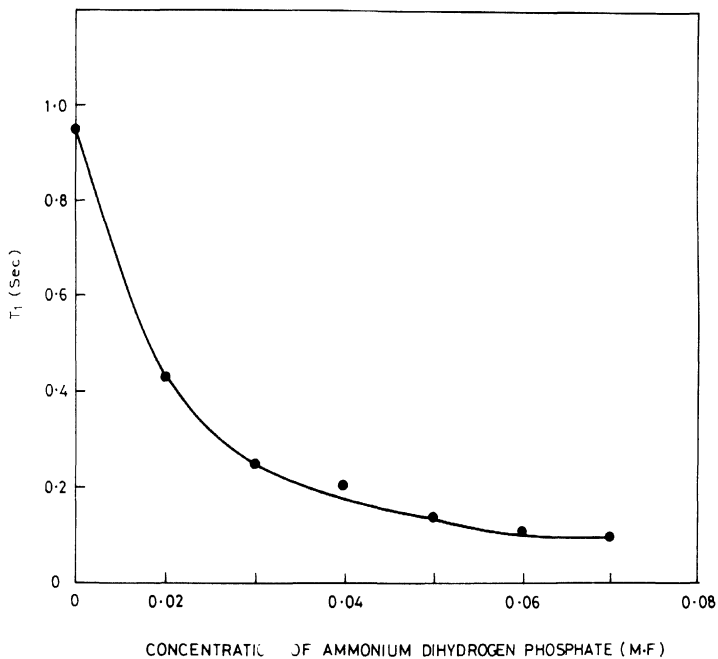


FIG-5-12. RELAXATION TIME (T_1) VS CONCENTRATION OF AMMONIUM DIHYDROGEN PHOSPHATE (M-F)

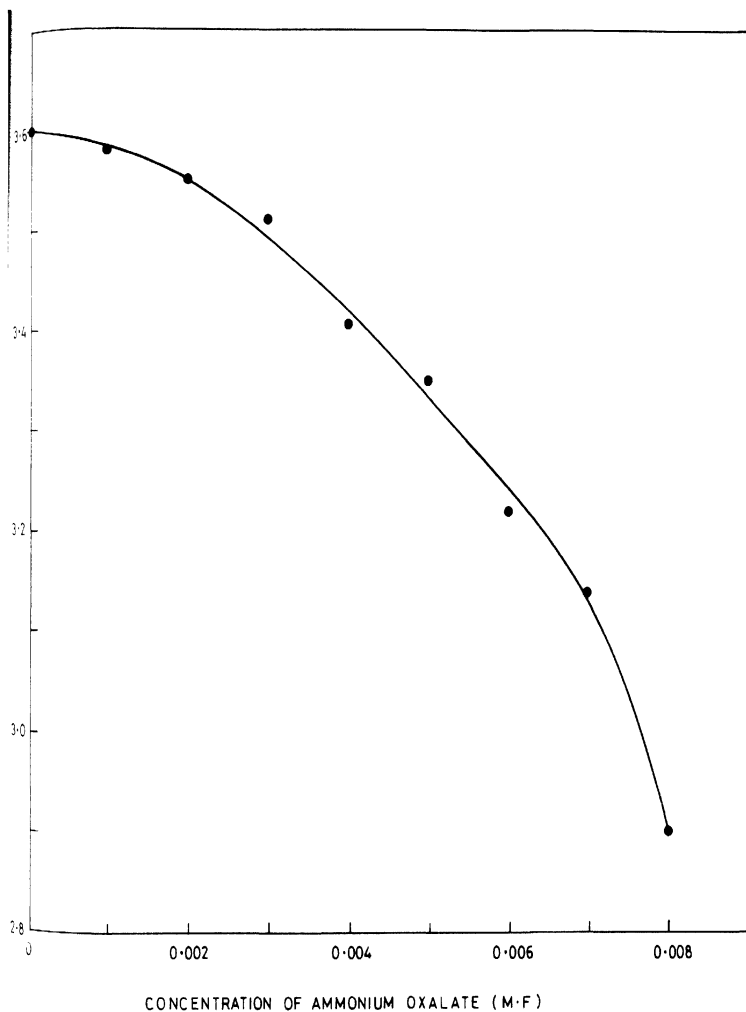


FIG-5-13. RELAXATION TIME (T_1) VS CONCENTRATION OF AMMONIUM OXALATE (M·F)

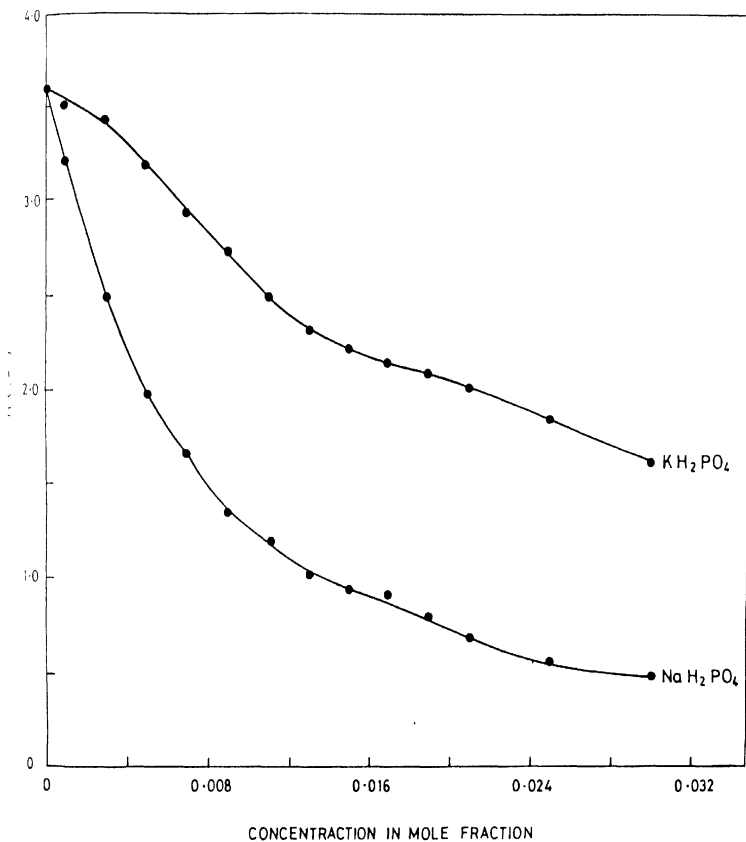


FIG-5-14. RELAXATION TIME (T_1) VS CONCENTRATION OF SODIUM AND POTASSIUM DIHYDROGEN PHOSPHATE (M·F)

concentration. It is clear from the calculated values of hydration number for these aqueous electrolytes. The calculated value of hydration number is larger for sodium di-hydrogen phosphate than potassium di-hydrogen phosphate at any particular concentration, thus supporting the above discussion for velocity variation with increasing concentration of these aqueous electrolytes.

5.3 NUCLEAR MAGNETIC RELAXATION STUDIES

The spin-lattice relaxation time and spin-spin relaxation times (T_1 and T_2) were measured at an RF frequency of 20 MHz using Bruker PC-120 NMR process analyser. The 'Inversion Recovery and Carr-Purcell-Meiboom-Gill programs were used for the measurement of T_1 and T_2 . 3-fold accumulation was used for the reduction of error, which was usually less than 2%. The measurements were carried out at a temperature of 303K.

The variation of relaxation times (T_1 and T_2) for aqueous solutions of ammonium chloride, ammonium oxalate, ammonium di-hydrogen phosphate, sodium di-hydrogen phosphate and potassium di-hydrogen phosphate for different solute concentrations are shown in figures 5.11 - 5.14 and in the tables 5.16-5.20. In aqueous solutions of ammonium chloride, the relaxation times decrease with increase of solute concentration. The other electrolytes also follow a similar behaviour with increase of solute concentration.

Among the group-I electrolytes, the decrease in the value of relaxation times is larger for ammonium di-hydrogen phosphate compared to ammonium chloride. Among the group-II electrolytes, the decrease in the value of relaxation times is larger for sodium di-hydrogen phosphate than potassium di-hydrogen phosphate at any given concentration. To test whether the decay of magnetisation is mono-exponential or multi-exponential, the variation of magnetisation (M) with the time interval (t) for these aqueous electrolytic solutions was plotted. From the plot it was found that, the decay of magnetisation is mono-exponential and hence we have a unique T_1 or T_2 value. The general change observed in the values of T_1 and T_2 with increase of solute concentration may be understood by the water structure making and breaking properties of the solute [15].

The earlier nuclear magnetic relaxation studies in aqueous solutions of fructose [15] and rare earth chlorides [16] established that the water structure breakers increases the value of relaxation time T_1 , whereas water structure makers have a tendency to decrease the relaxation times. Proton magnetic relaxation studies in several alcohols reveals that the relaxation times T_1 and T_2 decreases with increase of hydrogen bond energy [17].

It is very well established that the cations NH_4^+ and K^+ are water structure breakers [11], so one would expect T_1 and T_2 to increase with increase of solute concentration of ammonium chloride, ammonium oxalate, ammonium di-hydrogen phosphate and potassium di-hydrogen phosphate. But in the

present study, the relaxation times T_1 and T_2 decreases with increase of solute concentration, which may be qualitatively explained by resorting to Flickering Cluster model [10]. On the basis of this model, the NH_4^+ and K^+ ions break the open structure of water, resulting in the formation of hydration shells. The increased hydration in aqueous solutions of electrolytes decrease the freedom of movement of water molecules. This hydration may be the cause for the observed decrease in the values of relaxation times in the aqueous solutions of ammonium chloride, ammonium oxalate, ammonium di-hydrogen phosphate and potassium di-hydrogen phosphate [18]. The decrease in the values of T_1 in aqueous solutions of sodium di-hydrogen phosphate may be due to the water structure making property of Na^+ ions.

From the figure 5.14 it can be seen that the decrease in the value of T_1 is quite large for sodium di-hydrogen phosphate as compared to potassium di-hydrogen phosphate for any solute concentration. This may be attributed to the difference in the charge densities of Na^+ and K^+ ions. Due to the high charge density of Na^+ ion, a large number of water molecules are hydrated to Na^+ ion than K^+ ion.

The variation of spin-spin relaxation time T_2 of the aqueous solutions of electrolytes follow a similar behaviour as that of spin-lattice relaxation time (T_1). Hence the explanation proposed for the variation of T_1 appears to be valid for this case also.

These nuclear magnetic relaxation studies supports the ultrasonic velocity studies undertaken in the aqueous

solutions of ammonium chloride, ammonium oxalate, ammonium di-hydrogen phosphate, sodium di-hydrogen phosphate and potassium di-hydrogen phosphate.

5.4 ULTRASONIC ABSORPTION STUDIES

5.4.1 Introduction

Earlier ultrasonic absorption studies in aqueous electrolytes have been conducted with the main motivation of studying the abnormal absorption exhibited by several electrolytes in aqueous solutions [19-22]. For aqueous solutions of sodium bromide, sodium acetate and potassium acetates, the observed value of ultrasonic absorption was found to be less than that of pure water. This was evident from the ultrasonic absorption measurements of Barret and Beyer [23], Kurtz and Tamm [21] and Barret et al [24]. In aqueous sodium and potassium acetates, the absorption coefficient was found to have a considerably higher value at lower frequencies, whereas at a higher frequency it was found to decrease to a value lesser than that for pure solvent [19]. The magnitude of this decrease in absorption with increasing frequency was also found to be increasing with increasing electrolyte concentration.

From the present ultrasonic velocity studies, it can be seen that the ultrasonic velocities in aqueous solutions of ammonium chloride, ammonium oxalate, ammonium di-hydrogen phosphate, sodium di-hydrogen phosphate and potassium di-hydrogen phosphate increase non-linearly with increase in solute concentrations. In order to understand the molecular

dynamics completely, the parameters like structural viscosity and ultrasonic relaxation time are also to be evaluated. The ultrasonic absorption studies will be more useful in elucidating these parameters which may further help to understand the nature of solute-solvent interactions in these systems.

The absorption measurements were carried out in this laboratory using pulse-echo interferometer. Pulse technique was originally developed from radar principles by Pellam and Galt [25] and Pinkerton [26]. This is a most widely used technique for the study of ultrasonic propagation in liquids and solids.

The solutions were prepared with the solute concentrations in the same way as it was done for velocity studies. The ultrasonic absorptions were measured as detailed in the earlier chapter at room temperature (303 ± 0.1 K). Viscosities and densities were also determined as explained earlier. Using the values of ultrasound absorption, shear viscosity and density of the solution, the related parameters are calculated as detailed below.

The classical absorption is calculated using the relation (1.14). The excess absorption is estimated as the difference between the observed absorption and the classical absorption. Volume viscosity which is due to the structure of the liquid is calculated using the relation (1.18).

The variation of ultrasonic absorption and the calculated parameters with concentration of aqueous electrolytes are shown in tables 5.21-5.25. The variation

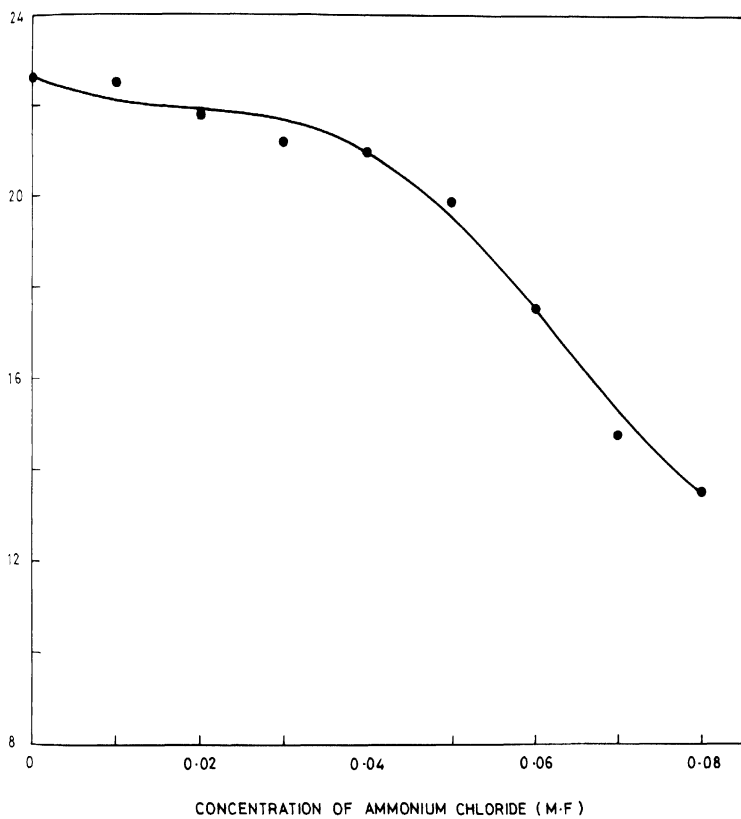


FIG-5-15. OBSERVED ABSORPTION VS CONCENTRATION OF AMMONIUM CHLORIDE (M·F)

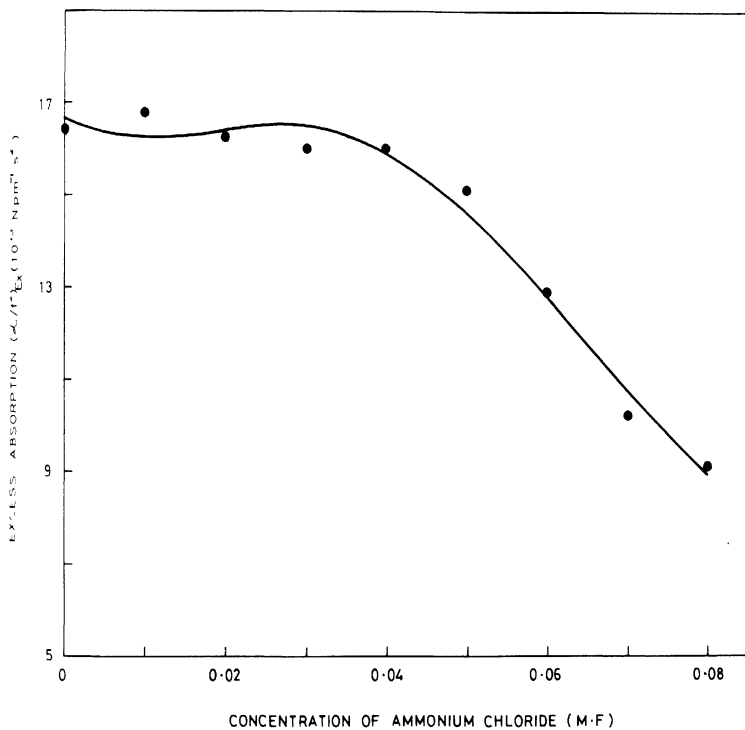


FIG-5-16. EXCESS ABSORPTION VS CONCENTRATION OF AMMONIUM CHLORIDE (M·F)

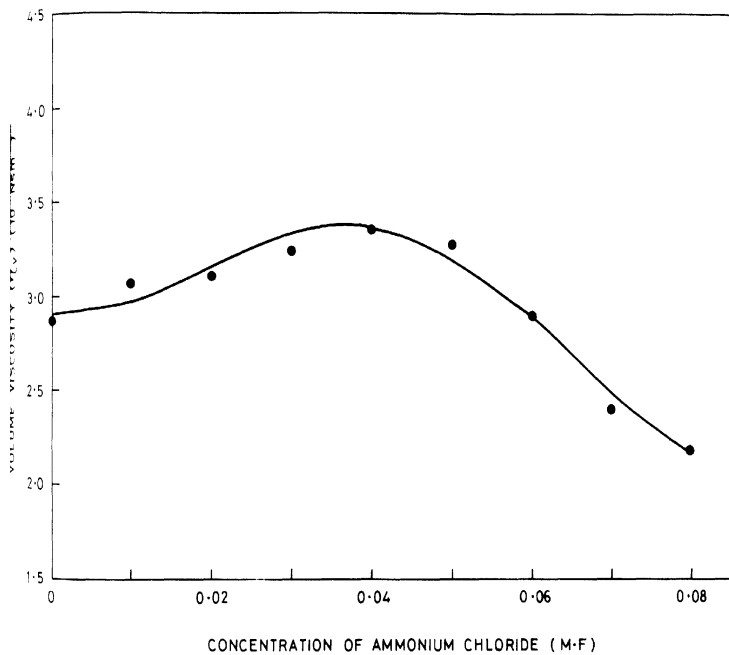


FIG-5-17. VOLUME VISCOSITY VS CONCENTRATION OF AMMONIUM
CHLORIDE (M·F)

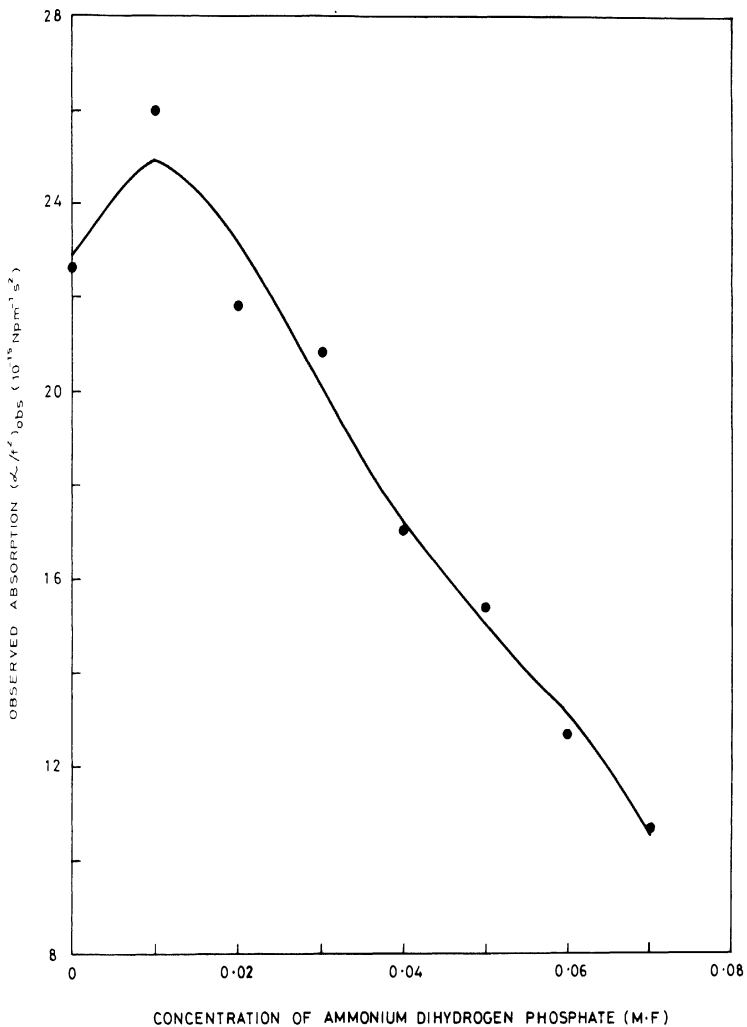


FIG.5.18. OBSERVED ABSORPTION VS CONCENTRATION OF AMMONIUM DIHYDROGEN PHOSPHATE (M·F)

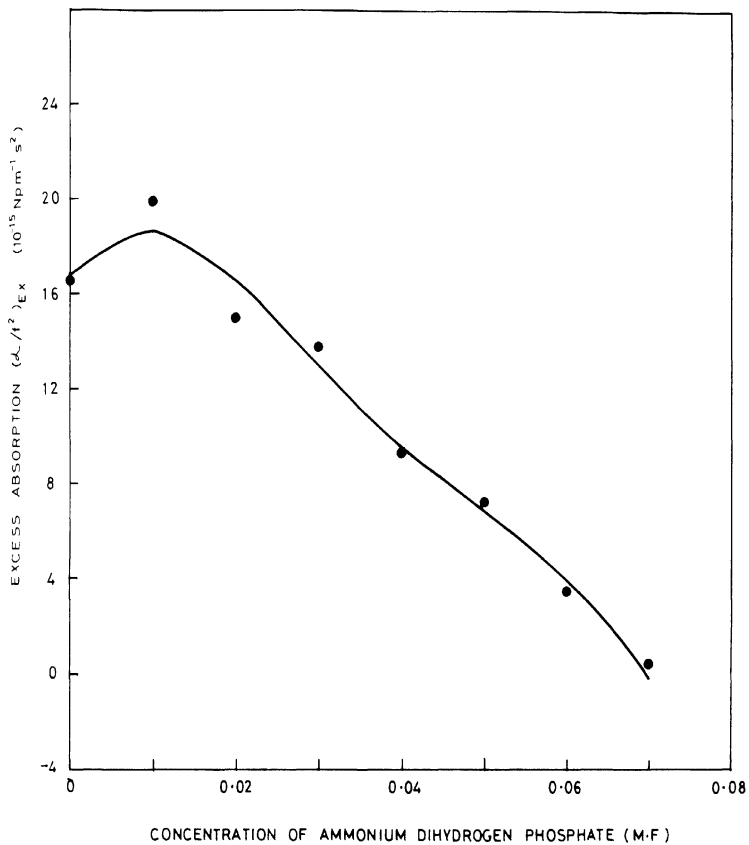


FIG-5-19 EXCESS ABSORPTION VS CONCENTRATION OF AMMONIUM
DIHYDROGEN PHOSPHATE

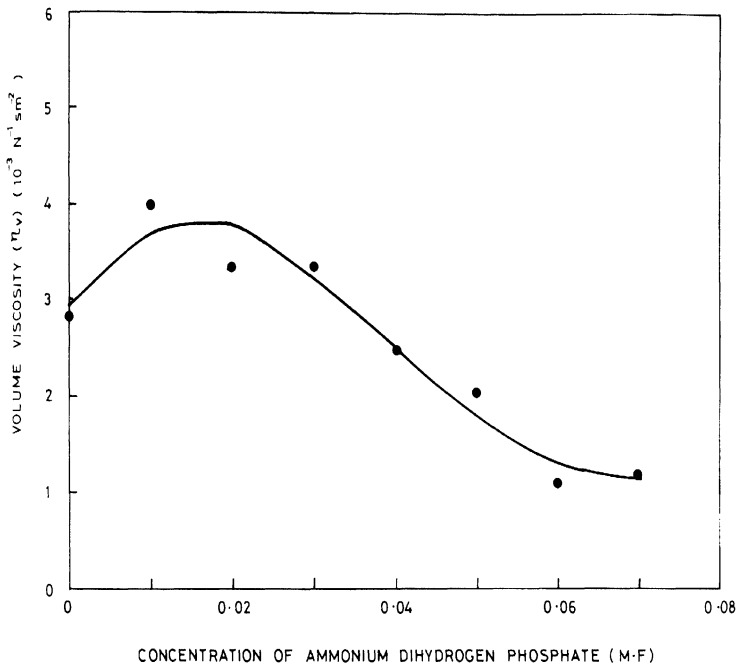


FIG.5.20. VOLUME VISCOSITY VS CONCENTRATION OF AMMONIUM
DIHYDROGEN PHOSPHATE (M.F)

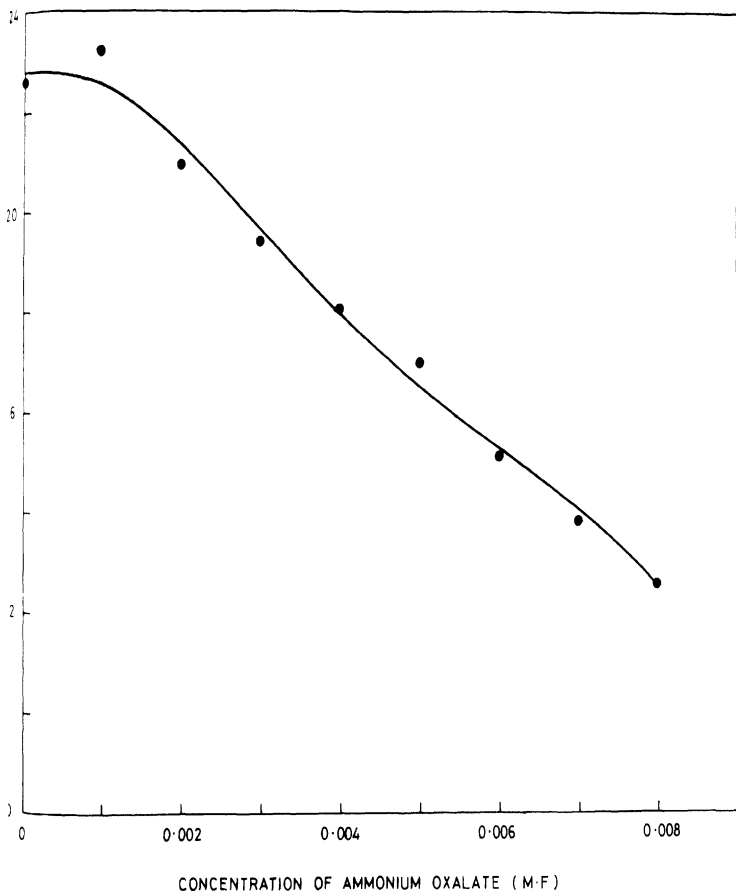


FIG-5-21 OBSERVED ABSORPTION VS CONCENTRATION OF AMMONIUM OXALATE (M·F)

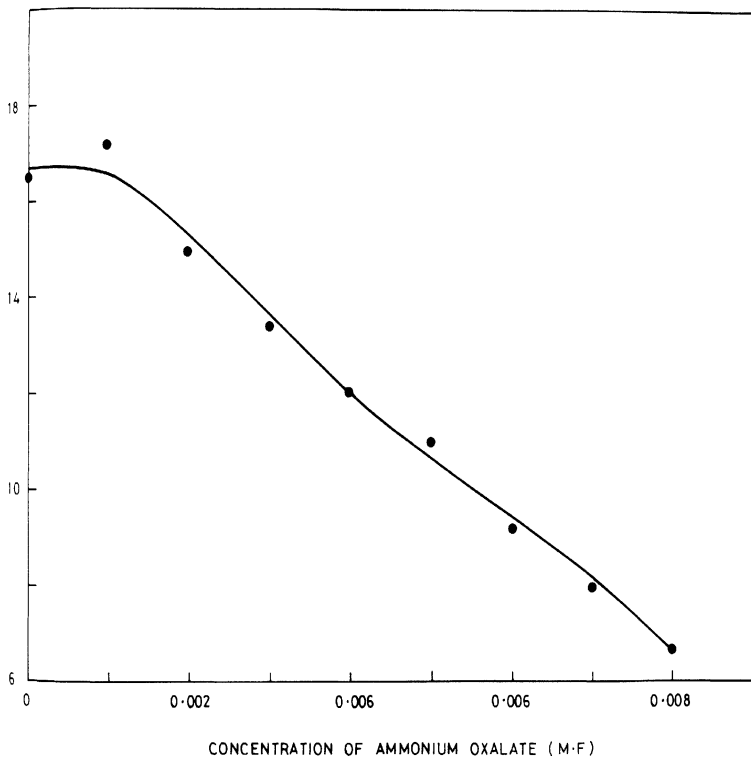


FIG-5-22. EXCESS ABSORPTION VS CONCENTRATION OF AMMONIUM OXALATE (M·F)

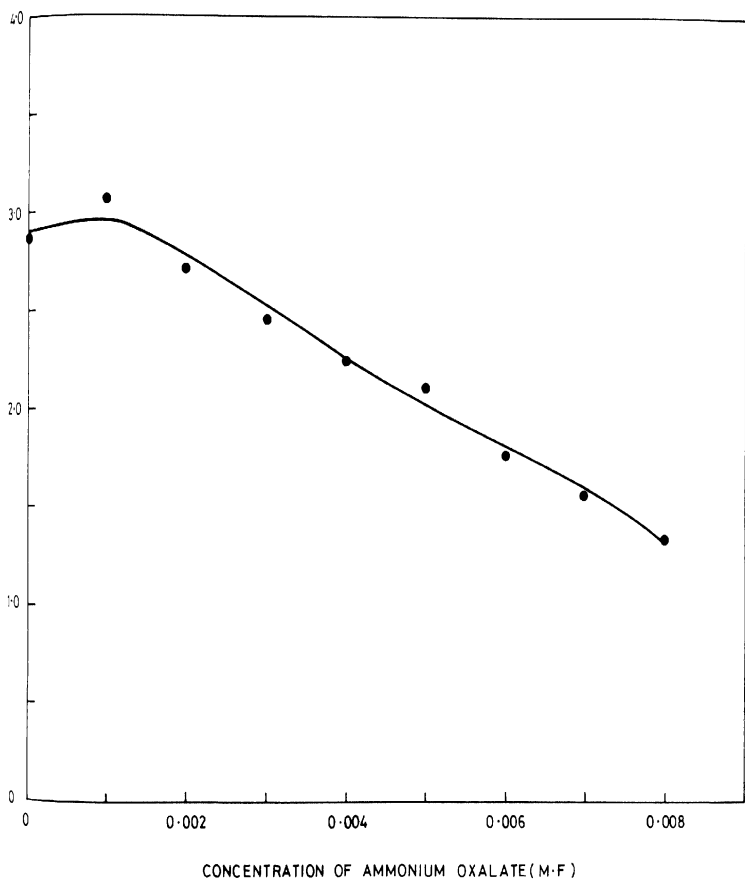
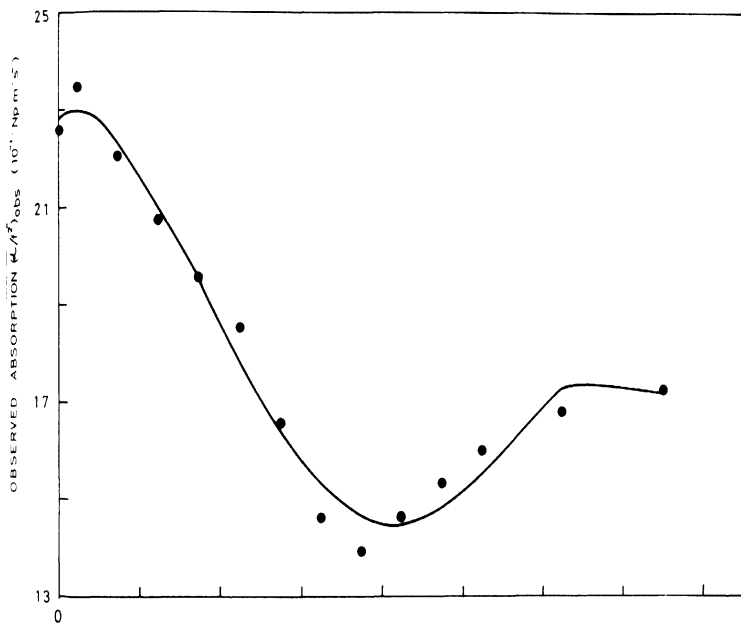


FIG-5-23. VOLUME VISCOSITY VS CONCENTRATION OF AMMONIUM OXALATE (M·F)



CONCENTRATION OF SODIUM DIHYDROGEN PHOSPHATE (M·F)

FIG-5-24. OBSERVED ABSORPTION VS CONCENTRATION OF SODIUM
DIHYDROGEN PHOSPHATE (M·F)

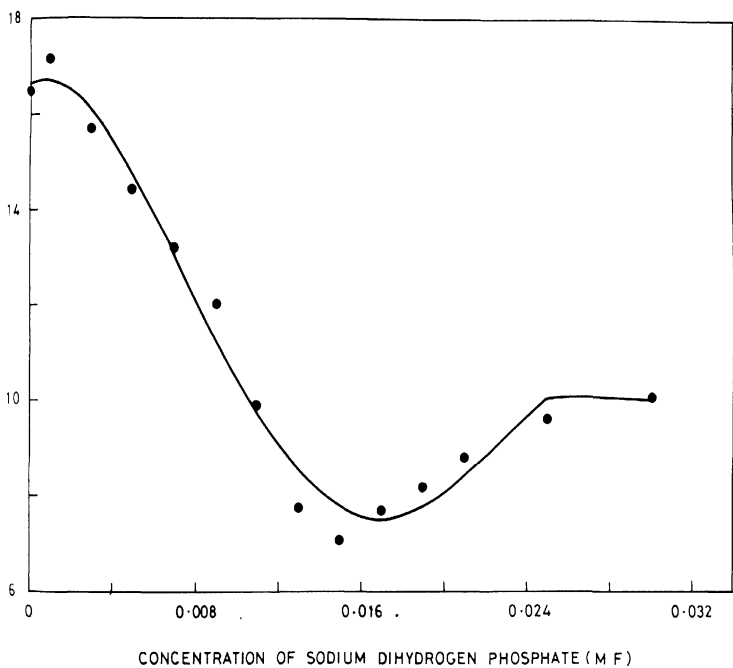


FIG-5-25. EXCESS ABSORPTION VS CONCENTRATION OF SODIUM DIHYDROGEN PHOSPHATE (M·F)

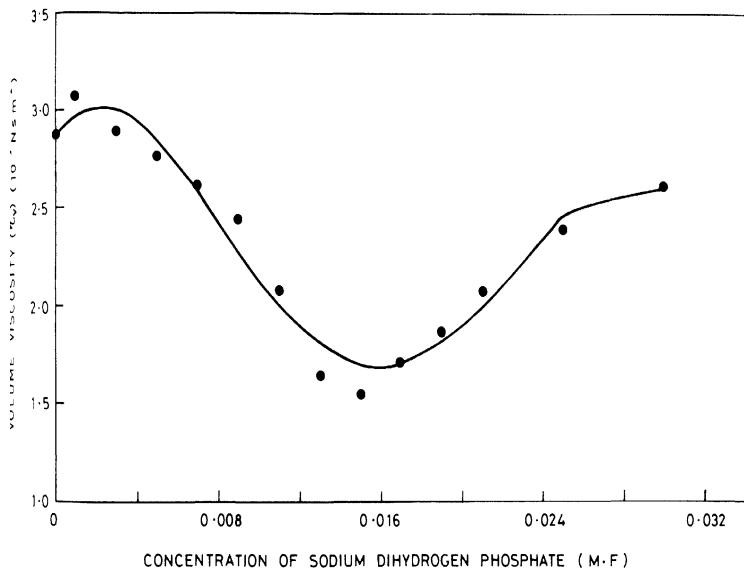


FIG-5-26. VOLUME VISCOSITY VS CONCENTRATION OF SODIUM DIHYDROGEN PHOSPHATE (M F)

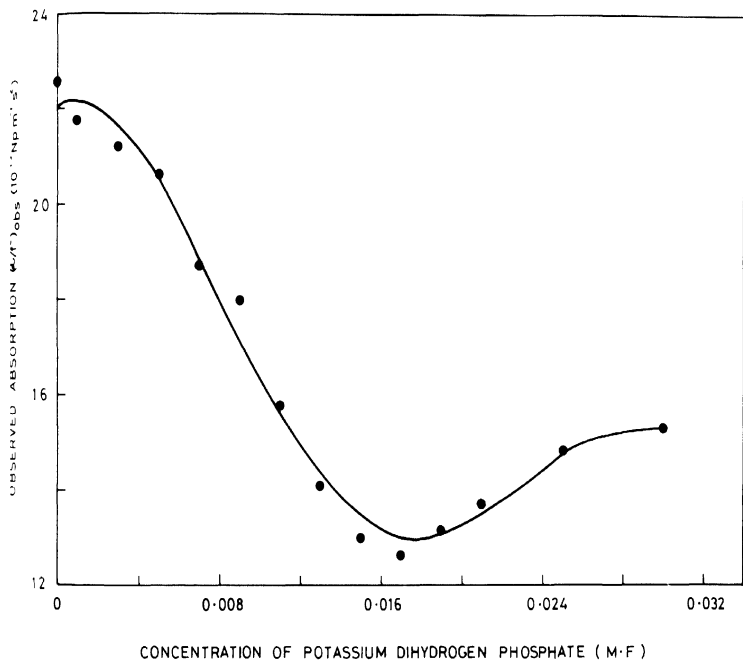


FIG-5-27. OBSERVED ABSORPTION VS CONCENTRATION OF POTASSIUM DIHYDROGEN PHOSPHATE (M·F)

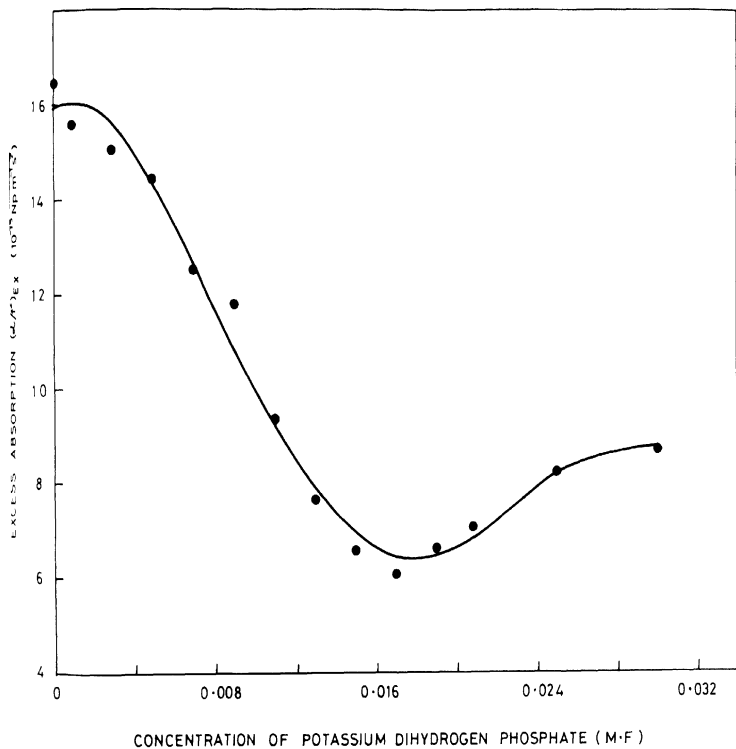


FIG-5-28. EXCESS ABSORPTION VS CONCENTRATION OF POTASSIUM DIHYDROGEN PHOSPHATE (M·F)

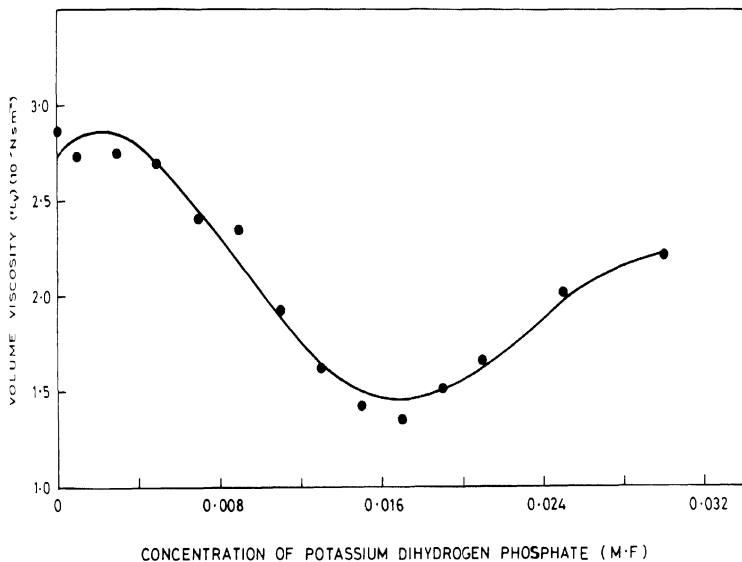


FIG-5-29. VOLUME VISCOSITY VS CONCENTRATION OF POTASSIUM DIHYDROGEN PHOSPHATE (M.F)

of observed absorption, excess absorption and volume viscosity with the solute concentration are shown graphically from figures 5.15-5.29. All the data were fitted to a suitable polynomial using the basic program "POLY" given in appendix - II.

5.4.2 Results and Discussion

It can be seen from the figures 5.15, 5.18, 5.21, 5.24 and 5.27 that the ultrasonic absorption decreases below the absorption value of water with increasing concentrations of ammonium chloride, ammonium di-hydrogen phosphate, ammonium oxalate, sodium di-hydrogen phosphate and potassium di-hydrogen phosphate. It can be seen from figures 5.15, 5.18 and 5.21 that, the observed absorption in aqueous ammonium chloride, ammonium di-hydrogen phosphate and ammonium oxalate decreases non-linearly with increase in concentration. However figure 5.24 shows that observed ultrasonic absorption for aqueous solutions of sodium di-hydrogen phosphate initially decreases with increase in concentration and attains a minimum value at a solute concentration of 0.015 mole fraction, then increases for further increase of solute concentration. A similar behaviour was observed for aqueous potassium di-hydrogen phosphate (fig. 5.27) with the exception that the absorption minimum occurs at different solute concentration i.e at 0.017 mole fraction.

The variation of excess absorption with concentration of ammonium chloride, ammonium di-hydrogen phosphate and

ammonium oxalate are shown in figures 5.16, 5.19 and 5.22. From these figures it is observed that the excess absorption decrease with increase of concentration of electrolytes. From the figures 5.25 and 5.28, it can be seen that the excess absorption for aqueous sodium di-hydrogen phosphate and potassium di-hydrogen phosphate initially decreases up to the concentrations of 0.015 mole fraction and 0.017 mole fraction and then increases for further increase of solute concentration. The variation of volume viscosity and relaxation time for these electrolytes are shown in tables 5.21-5.25. The variation of volume viscosity and relaxation time follows the same trend as that of observed absorption for these aqueous electrolytes.

Among the group-I electrolytes, the decrease in the observed absorption is largest for ammonium oxalate in spite of its low solubility in water. It is larger for ammonium di-hydrogen phosphate compared to ammonium chloride. In group-II electrolytes, the decrease in the absorption is more for potassium di-hydrogen phosphate compared to sodium di-hydrogen phosphate.

The salient features of the absorption study are summarised as follows:

1. The observed ultrasonic absorption decreases below the absorption value of water with increasing concentration of ammonium chloride, ammonium di-hydrogen phosphate and ammonium oxalate.

2. Observed ultrasonic absorptions for aqueous sodium di-hydrogen phosphate and potassium di-hydrogen phosphate solutions initially decreases with increase in concentration and reach minimum values at a solute concentrations of 0.015 and 0.017 mole fractions respectively and subsequently increases for further increase of solute concentrations.
3. The excess absorptions of ammonium chloride, ammonium di-hydrogen phosphate and ammonium oxalate also decrease with increasing concentration of electrolytes.
4. The excess absorptions of sodium di-hydrogen phosphate and potassium di-hydrogen phosphate follow a similar trend as that of observed absorption variation.
5. Among group-I electrolytes, the decrease in the observed absorption with increasing concentration of electrolyte is largest for ammonium oxalate. But it is larger for ammonium di-hydrogen phosphate compared to ammonium chloride.
6. Among group-II electrolytes, the decrease in observed absorption is more for potassium di-hydrogen phosphate compared to sodium di-hydrogen phosphate.
7. The variations in volume viscosity and relaxation time also follow a similar behaviour as the observed absorption with increasing solute concentration of electrolytes.

The variation of observed absorption with increase in solute concentrations of the electrolytes is shown in figures 5.15, 5.18, 5.21, 5.24 and 5.27. This variation of excess absorption as a function of concentration of electrolytes may be explained as follows. The addition of an electrolyte to a polar solvent can have two effects [27];

1. The ions act as acceptors and they can compete with the protons for the lone pair of electrons on the oxygen. This leads to the formation of solvation sheath around the ion.
2. The ion may possess a large volume and hence a small effective charge density. The equilibrium between the two structural forms is disturbed.

Both these effects contribute leading to a change in the acoustic absorption.

According to Endo and Nomoto [28] the non-hydrated portion of the liquid water (free water) decreases with increasing concentration, leading to a decrease in the sound absorption. This explanation also holds good for the decrease in the absorption observed in the present studies on ammonium chloride, ammonium di-hydrogen phosphate and ammonium oxalate. For sodium di-hydrogen phosphate and potassium di-hydrogen phosphate, the above explanation holds good till the minimum observed.

The variation of excess absorption can also be explained by Hall's two state model of water [29]. According to this model, water is considered to be mixture

of two molecular species. One of them has open ice like structure while the other has more densely packed structure. The addition of electrolytes to water may shift the equilibrium between the two configurations, resulting in reduction of excess absorption of the solution. This may result in a reduction of potential barrier between the two structural forms of water molecules particularly in the vicinity of the ions. This would reduce the relaxation time and may lead to the decrease of excess absorption at frequencies well below the relaxation frequency [30].

Among the group-I electrolytes, the decrease in the excess absorption with increasing concentration of the electrolyte is largest for ammonium oxalate in spite of its low solubility. It is larger for ammonium di-hydrogen phosphate compared to ammonium chloride. Since the cations NH_4^+ being the same in these electrolytes, the difference in the decrease of observed absorption may be mainly due to the anions (namely chloride, phosphate and oxalate ions) provided the solvent-solvent interactions are similar. Hence this difference in the observed absorption may be attributed to the difference in charge densities of the anions [24].

However, in aqueous solutions of sodium di-hydrogen phosphate and potassium di-hydrogen phosphate, since the anion being the same this difference may be attributed to the difference in charge densities of cations. The increase in the observed absorption after 0.015 mole fraction of sodium di-hydrogen phosphate may probably due to a

consequence of the introduction of a new structural contribution to the relaxation at high ionic strength [27]. The same explanation holds good for the observed increase of ultrasonic absorption after 0.017 mole fraction of potassium di-hydrogen phosphate.

In conclusion, it can be seen that the observed decrease in the absorption to a value below that of water with increasing concentration of electrolytes may be due to the difference in their charge densities, which contribute more to the increasing rates of conversion between the two structural forms of water. The decrease may also be due to the decrease in the non-hydrated water (free water) which mainly contribute for the absorption. The increase in the observed absorption at high concentrations of sodium and potassium di-hydrogen phosphates may probably due to a consequence of the introduction of a new structural contribution to the relaxation at high ionic strength. .

TABLE - 5.1

Ultrasonic velocity and related parameters in aqueous solutions of ammonium chloride at 303 K.

Mole fraction X	Kgm^{-3} ρ	ms^{-1} C	$10^{-10}\text{N}^{-1}\text{m}^2$ β_s	10^{-4}Nsm^{-2} η_s	A^0 L_f	h
Water	995.65	1510.00	4.405	7.98	0.419	-
0.01	1007.21	1531.27	4.234	7.87	0.411	3.86
0.02	1013.10	1547.62	4.121	7.95	0.405	3.18
0.03	1019.48	1575.08	3.954	7.84	0.397	3.32
0.04	1023.50	1590.05	3.864	7.87	0.392	2.95
0.05	1031.58	1608.57	3.758	7.89	0.387	2.80
0.06	1037.93	1622.06	3.662	7.98	0.382	2.64
0.07	1043.64	1639.09	3.567	8.03	0.377	2.53
0.08	1047.33	1650.97	3.503	8.04	0.374	2.36

X - concentration of ammonium chloride in mole fraction;

ρ - density of the solution;

C - ultrasonic velocity;

β_s - adiabatic compressibility;

η_s - shear viscosity;

L_f - intermolecular free length;

h - hydration number

TABLE - 5.2

Ultrasonic velocity and related parameters in aqueous solutions of ammonium chloride at 313 K.

Mole fraction X	Kgm^{-3} ρ	ms^{-1} C	$10^{-10} \text{N}^{-1} \text{m}^2$ β_s	10^{-4}Nsm^{-2} η_s	A^0 L_f
Water	992.22	1528.86	4.312	6.53	0.422
0.01	1002.52	1546.95	4.168	6.69	0.415
0.02	1010.56	1564.26	4.044	6.77	0.408
0.03	1017.62	1582.71	3.923	6.85	0.402
0.04	1023.09	1601.85	3.809	6.94	0.396
0.05	1028.40	1619.64	3.707	7.01	0.391
0.06	1033.46	1636.41	3.613	7.04	0.386
0.07	1038.39	1649.80	3.538	7.10	0.381
0.08	1042.51	1658.93	3.485	7.12	0.379

X - concentration of ammonium chloride in mole fraction;

ρ - density of the solution;

C - ultrasonic velocity;

β_s - adiabatic compressibility;

η_s - shear viscosity;

L_f - intermolecular free length

TABLE - 5.3

Ultrasonic velocity and related parameters in aqueous solutions of ammonium chloride at 323 K.

Mole fraction X	Kgm^{-3} ρ	ms^{-1} C	$10^{-10} \text{N}^{-1} \text{m}^2$ β_s	10^{-4}Nsm^{-2} η_s	A^0 L_f
Water	988.04	1542.55	4.254	5.47	0.425
0.01	997.88	1562.37	4.105	5.65	0.418
0.02	1005.15	1576.32	4.004	5.74	0.413
0.03	1014.36	1593.71	3.881	5.79	0.406
0.04	1021.14	1613.13	3.763	5.80	0.400
0.05	1025.69	1631.78	3.862	5.81	0.395
0.06	1026.83	1649.12	3.581	5.84	0.390
0.07	1029.82	1662.00	3.515	5.92	0.387
0.08	1040.97	1666.97	3.453	6.06	0.384

X - concentration of ammonium chloride in mole fraction;

ρ - density of the solution;

C - ultrasonic velocity;

β_s - adiabatic compressibility;

η_s - shear viscosity;

L_f - intermolecular free length

TABLE - 5.4

Ultrasonic velocity and related parameters in aqueous solutions of ammonium oxalate at 303 K.

Mole fraction X	Kgm^{-3} ρ	ms^{-1} C	$10^{-10} \text{N}^{-1} \text{m}^2$ β_s	$10^{-4} \text{Ncm}^{-2} \text{A}^0$ η_s	A^0 L_f	h
Water	995.65	1510.00	4.405	7.98	0.419	-
0.001	998.61	1519.27	4.338	8.07	0.416	15.20
0.002	1000.98	1528.23	4.278	8.16	0.413	14.35
0.003	1004.54	1531.45	4.245	8.27	0.411	12.08
0.004	1008.39	1541.39	4.174	8.41	0.408	13.05
0.005	1011.06	1549.71	4.118	8.46	0.405	12.97
0.006	1014.32	1552.89	4.088	8.60	0.403	11.91
0.007	1016.69	1563.97	4.021	8.73	0.400	12.37
0.008	1019.65	1569.82	3.980	8.88	0.398	11.97

X - concentration of ammonium oxalate in mole fraction;
 ρ - density of the solution; C - ultrasonic velocity;
 β_s - adiabatic compressibility; η_s - shear viscosity;
 L_f - intermolecular free length; h - hydration number

TABLE - 5.5

Ultrasonic velocity and related parameters in aqueous solutions of ammonium oxalate at 313 K.

Mole fraction X	Kgm^{-3} ρ	ms^{-1} C	$10^{-10} \text{N}^{-1} \text{m}^2$ β_s	10^{-4}Nsm^{-2} η_s	A^0 L_f
Water	992.22	1528.86	4.312	6.53	0.422
0.001	995.14	1538.26	4.247	6.60	0.418
0.002	998.18	1547.26	4.185	6.69	0.415
0.003	1001.31	1554.62	4.132	6.79	0.412
0.004	1004.35	1559.55	4.094	6.88	0.410
0.005	1007.48	1564.66	4.054	6.98	0.408
0.006	1010.41	1570.82	4.011	7.08	0.406
0.007	1013.29	1577.78	3.964	7.17	0.404
0.008	1016.22	1586.76	3.908	7.24	0.401

X - concentration of ammonium oxalate in mole fraction;
 ρ - density of the solution; C - ultrasonic velocity;
 β_s - adiabatic compressibility; η_s - shear viscosity;
 L_f - intermolecular free length

TABLE - 5.6

Ultrasonic velocity and related parameters in aqueous solutions of ammonium oxalate at 323 K.

Mole fraction X	Kgm^{-3} ρ	ms^{-1} C	$10^{-10}\text{N}^{-1}\text{m}^2$ β_s	10^{-4}Nsm^{-2} η_s	A^0 L_f
Water	988.04	1542.55	4.254	5.47	0.425
0.001	991.55	1548.86	4.204	5.51	0.423
0.002	994.81	1556.69	4.148	5.57	0.420
0.003	997.88	1563.85	4.098	5.64	0.417
0.004	1000.76	1568.81	4.060	5.70	0.415
0.005	1003.54	1574.18	4.021	5.76	0.413
0.006	1006.20	1580.65	3.978	5.83	0.411
0.007	1008.84	1587.16	3.935	5.90	0.409
0.008	1011.94	1594.56	3.887	5.95	0.406

X - concentration of ammonium oxalate in mole fraction;

ρ - density of the solution;

C - ultrasonic velocity;

β_s - adiabatic compressibility;

η_s - shear viscosity;

L_f - intermolecular free length

TABLE - 5.7

Ultrasonic velocity and related parameters in aqueous solutions of ammonium di-hydrogen phosphate at 303 K

Mole fraction X	Kgm^{-3} ρ	ms^{-1} C	$10^{-10}\text{N}^{-1}\text{m}^2$ β_s	10^{-4}Nsm^{-2} η_s	A^0 L_f	h
Water	995.85	1510.00	4.405	7.98	0.419	-
0.01	1038.94	1585.53	3.935	9.35	0.398	10.58
0.02	1061.89	1601.97	3.670	10.89	0.382	8.18
0.03	1090.11	1633.38	3.438	12.74	0.370	7.10
0.04	1116.84	1665.54	3.228	14.98	0.359	6.42
0.05	1144.76	1700.40	3.021	17.52	0.347	5.97
0.06	1168.52	1714.26	2.912	20.50	0.341	5.31
0.07	1187.24	1716.65	2.858	23.43	0.337	4.67

X - concentration of ammonium di-hydrogen phosphate in mole fraction;

ρ - density of the solution;

C - ultrasonic velocity;

β_s - adiabatic compressibility;

η_s - shear viscosity;

L_f - intermolecular free length;

h - hydration number

TABLE - 5.8

Ultrasonic velocity and related parameters in aqueous solutions of ammonium di-hydrogen phosphate at 313 K

Mole fraction X	Kgm^{-3} ρ	ms^{-1} C	$10^{-10} \text{N}^{-1} \text{m}^2$ β_s	10^{-4}Nsm^{-2} η_s	\AA^0 L_f
Water	992.22	1528.86	4.312	6.53	0.422
0.01	1025.67	1573.81	3.936	7.36	0.402
0.02	1056.56	1608.93	3.656	8.75	0.388
0.03	1084.87	1643.06	3.414	9.61	0.375
0.04	1111.41	1680.77	3.185	11.06	0.362
0.05	1135.66	1711.50	3.006	12.90	0.351
0.06	1158.48	1726.61	2.895	14.90	0.345
0.07	1180.07	1741.78	2.793	18.78	0.339

X - concentration of ammonium di-hydrogen phosphate in mole fraction;

ρ - density of the solution;

C - ultrasonic velocity;

β_s - adiabatic compressibility;

η_s - shear viscosity;

L_f - intermolecular free length

TABLE - 5.9

Ultrasonic velocity and related parameters in aqueous solutions of ammonium di-hydrogen phosphate at 323 K

Mole fraction X	Kgm^{-3} ρ	ms^{-1} C	$10^{-10}\text{N}^{-1}\text{m}^2$ β_s	10^{-4}Nsm^{-2} η_s	A^0 L_f
Water	988.04	1542.55	4.254	5.47	0.425
0.01	1020.87	1578.98	3.929	6.29	0.409
0.02	1050.74	1618.33	3.643	7.18	0.394
0.03	1078.52	1654.18	3.388	8.15	0.380
0.04	1104.91	1693.44	3.160	9.24	0.367
0.05	1130.17	1723.50	2.979	10.67	0.356
0.06	1154.01	1740.11	2.862	12.67	0.349
0.07	1176.35	1756.00	2.757	15.17	0.342

X - concentration of ammonium di-hydrogen phosphate in mole fraction;

ρ - density of the solution;

C - ultrasonic velocity;

β_s - adiabatic compressibility;

η_s - shear viscosity;

L_f - intermolecular free length

TABLE - 5.10

Ultrasonic velocity and related parameters in aqueous solutions of sodium di-hydrogen phosphate at 303 K

Mole fraction	Kgm^{-3}	ms^{-1}	$10^{-10} \text{N}^{-1} \text{m}^2$	10^{-4}Nsm^{-2}	A^0	h
X	ρ	C	β_s	η_s	L_f	
Water	995.65	1510.00	4.405	7.97	0.419	-
0.001	1009.33	1517.37	4.303	8.45	0.414	23.24
0.003	1019.59	1529.45	4.193	8.85	0.409	15.98
0.005	1028.60	1544.15	4.077	9.16	0.403	14.80
0.007	1038.40	1557.21	3.971	9.48	0.398	13.99
0.009	1047.44	1568.00	3.883	9.99	0.393	13.04
0.011	1055.99	1571.32	3.835	10.30	0.391	11.64
0.013	1064.29	1579.23	3.787	10.86	0.387	11.00
0.015	1073.08	1590.04	3.686	11.20	0.383	10.72
0.017	1082.37	1597.50	3.620	11.68	0.380	10.31
0.019	1090.92	1605.71	3.555	12.22	0.376	9.96
0.021	1099.22	1617.75	3.476	12.63	0.372	9.83
0.025	1118.00	1640.00	3.326	13.46	0.364	9.55
0.030	1138.60	1649.62	3.233	13.88	0.359	8.60

X - concentration of sodium di-hydrogen phosphate in mole fraction;

ρ - density of the solution;

C - ultrasonic velocity;

β_s - adiabatic compressibility;

η_s - shear viscosity;

L_f - intermolecular free length;

h - hydration number

TABLE - 5.11

Ultrasonic velocity and related parameters in aqueous solutions of sodium di-hydrogen phosphate at 313 K

Mole fraction X	Kgm^{-3} ρ	ms^{-1} C	$10^{-10} \text{N}^{-1} \text{m}^2$ β_s	10^{-4}Nsm^{-2} η_s	A^0 L_f
Water	992.22	1528.86	4.312	6.53	0.422
0.001	997.19	1537.19	4.244	6.67	0.418
0.003	1007.94	1546.50	4.148	6.97	0.413
0.005	1018.54	1561.33	4.028	7.23	0.407
0.007	1028.36	1574.73	3.921	7.55	0.401
0.009	1038.88	1582.54	3.843	7.88	0.397
0.011	1048.09	1589.72	3.775	8.10	0.394
0.013	1056.31	1596.92	3.712	8.34	0.390
0.015	1067.14	1609.48	3.618	8.62	0.386
0.017	1077.11	1620.49	3.535	8.88	0.381
0.019	1085.53	1627.82	3.477	9.13	0.378
0.021	1094.48	1639.33	3.400	9.38	0.374
0.025	1111.91	1656.58	3.277	9.86	0.367
0.030	1132.68	1668.91	3.170	10.44	0.361

X - concentration of sodium di-hydrogen phosphate in mole fraction;

ρ - density of the solution;

C - ultrasonic velocity;

β_s - adiabatic compressibility;

η_s - shear viscosity;

L_f - intermolecular free length

TABLE - 5.12

Ultrasonic velocity and related parameters in aqueous solutions of sodium di-hydrogen phosphate at 323 K

Mole fraction X	Kgm^{-3} ρ	ms^{-1} C	$10^{-10} \text{N}^{-1} \text{m}^2$ β_s	10^{-4}Nsm^{-2} η_s	A^0 L_f
Water	986.04	1542.55	4.254	5.47	0.425
0.001	994.85	1551.34	4.177	5.57	0.421
0.003	1004.19	1560.91	4.087	5.77	0.417
0.005	1013.82	1575.47	3.974	5.96	0.411
0.007	1024.57	1589.77	3.862	6.19	0.405
0.009	1033.25	1597.78	3.791	6.42	0.401
0.011	1044.22	1606.25	3.712	6.62	0.397
0.013	1056.54	1611.94	3.643	6.85	0.394
0.015	1063.12	1623.42	3.569	7.11	0.390
0.017	1070.85	1636.98	3.485	7.38	0.385
0.019	1081.23	1644.94	3.418	7.66	0.382
0.021	1089.99	1652.88	3.358	7.97	0.378
0.025	1106.89	1673.08	3.227	8.65	0.370
0.030	1126.91	1689.26	3.110	9.66	0.364

X - concentration of sodium di-hydrogen phosphate in mole fraction;

ρ - density of the solution;

C - ultrasonic velocity;

β_s - adiabatic compressibility;

η_s - shear viscosity;

L_f - intermolecular free length

TABLE - 5.13

Ultrasonic velocity and related parameters in aqueous solutions of potassium di-hydrogen phosphate at 303K

Mole fraction	Kgm^{-3}	ms^{-1}	$10^{-10} \text{N}^{-1} \text{m}^2$	10^{-4}Nsm^{-2}	A^0	h
X	ρ	C	β_s	η_s	L_f	
Water	995.85	1510.00	4.405	7.97	0.419	-
0.001	1000.05	1512.92	4.369	8.11	0.417	8.21
0.003	1010.80	1523.86	4.262	8.34	0.412	10.77
0.005	1020.57	1532.00	4.175	8.62	0.408	10.40
0.007	1031.08	1541.97	4.079	8.88	0.403	10.49
0.009	1040.85	1555.85	3.969	9.14	0.398	10.89
0.011	1051.11	1565.19	3.883	9.84	0.393	10.66
0.013	1060.15	1575.71	3.799	10.19	0.389	10.45
0.015	1070.42	1586.42	3.712	10.46	0.384	10.33
0.017	1079.70	1593.36	3.648	10.87	0.381	9.94
0.019	1087.76	1603.93	3.574	11.13	0.377	9.74
0.021	1098.03	1611.30	3.508	11.50	0.374	9.50
0.025	1117.77	1629.00	3.371	11.86	0.366	9.15
0.030	1134.43	1641.49	3.271	12.61	0.361	8.33

X - concentration of potassium di-hydrogen phosphate in mole fraction;

ρ - density of the solution;

β_s - adiabatic compressibility;

L_f - intermolecular free length;

C - ultrasonic velocity;

η_s - shear viscosity;

h - hydration number

TABLE - 5.14

Ultrasonic velocity and related parameters in aqueous solutions of potassium di-hydrogen phosphate at 313 K

Mole fraction X	Kgm^{-3} ρ	ms^{-1} C	$10^{-10} \text{N}^{-1} \text{m}^2$ β_s	10^{-4}Nsm^{-2} η_s	A^0 L_f
Water	992.22	1528.86	4.312	6.53	0.422
0.001	996.85	1531.19	4.279	7.10	0.419
0.003	1006.78	1539.75	4.190	7.36	0.415
0.005	1016.55	1549.18	4.099	7.58	0.410
0.007	1026.23	1559.49	4.007	7.78	0.406
0.009	1035.82	1570.39	3.915	7.98	0.401
0.011	1045.32	1581.59	3.824	8.22	0.396
0.013	1054.87	1591.38	3.743	8.40	0.392
0.015	1064.05	1603.86	3.654	8.63	0.387
0.017	1073.27	1614.35	3.575	8.89	0.383
0.019	1082.41	1624.04	3.503	9.16	0.379
0.021	1091.61	1630.88	3.444	9.56	0.376
0.025	1109.26	1645.56	3.329	9.45	0.370
0.030	1130.92	1650.78	3.245	10.45	0.365

X - concentration of potassium di-hydrogen phosphate in mole fraction;
 ρ - density of the solution; C - ultrasonic velocity;
 β_s - adiabatic compressibility; η_s - shear viscosity;
 L_f - intermolecular free length

TABLE - 5.15

Ultrasonic velocity and related parameters in aqueous solutions of potassium di-hydrogen phosphate at 323 K

Mole fraction X	Kgm^{-3} ρ	ms^{-1} C	$10^{-10}\text{N}^{-1}\text{m}^2$ β_s	10^{-4}Nsm^{-2} η_s	A^0 L_f
Water	988.04	1542.55	4.254	5.47	0.425
0.001	993.59	1544.44	4.219	5.71	0.423
0.003	1003.15	1553.36	4.131	5.92	0.419
0.005	1012.93	1562.22	4.045	6.16	0.415
0.007	1022.59	1573.35	3.951	6.38	0.410
0.009	1032.13	1583.83	3.863	6.56	0.405
0.011	1041.55	1595.94	3.770	6.73	0.400
0.013	1051.09	1604.40	3.696	6.85	0.396
0.015	1060.07	1616.16	3.612	7.03	0.392
0.017	1069.19	1628.84	3.526	7.17	0.387
0.019	1078.22	1639.07	3.452	7.32	0.383
0.021	1087.16	1643.34	3.406	7.48	0.381
0.025	1104.83	1660.87	3.281	7.90	0.373
0.030	1126.46	1670.95	3.180	8.73	0.368

X - concentration of potassium di-hydrogen phosphate in mole fraction;
 ρ - density of the solution; C - ultrasonic velocity;
 β_s - adiabatic compressibility; η_s - shear viscosity;
 L_f - intermolecular free length

TABLE 5.16

Relaxation Times (T_1 and T_2) for aqueous solutions of ammonium chloride at 303 K.

Mole fraction X	T_1 sec	Error	T_2 sec	Error
Water	3.603	0.0324	2.823	0.0581
0.01	3.550	0.0333	0.821	0.0062
0.02	3.472	0.0180	0.525	0.0092
0.03	3.372	0.0220	0.412	0.0017
0.04	3.305	0.0366	0.361	0.0091
0.05	3.242	0.0163	0.346	0.0014
0.06	3.179	0.0281	0.313	0.0034
0.07	3.100	0.0192	0.304	0.0015
0.08	3.038	0.0311	0.298	0.0025

T_1 - spin-lattice relaxation time; T_2 - spin-spin relaxation time

TABLE 5.17

Relaxation Times (T_1 and T_2) for aqueous solutions of ammonium di-hydrogen phosphate at 303 K.

Mole fraction X	T_1 sec	Error	T_2 sec	Error
Water	3.6023	0.0324	2.8230	0.0581
0.01	0.9479	0.0101	0.4164	0.0093
0.02	0.4261	0.0043	0.3391	0.0468
0.03	0.2521	0.0025	0.1631	0.0074
0.04	0.2084	0.0008	0.1593	0.0126
0.05	0.1363	0.0009	0.1011	0.0046
0.06	0.1125	0.0095	0.0979	0.0076
0.07	0.0987	0.0005	0.0939	0.0003

T_1 - spin-lattice relaxation time; T_2 - spin-spin relaxation time

TABLE 5.18

Relaxation Times (T_1 and T_2) for aqueous solutions of ammonium oxalate at 303 K.

Mole fraction X	T_1 sec	Error	T_2 sec	Error
Water	3.6023	0.0324	2.8230	0.0581
0.001	3.5878	0.0385	2.5123	0.0282
0.002	3.5501	0.0305	2.4123	0.0344
0.003	3.5128	0.0262	2.3899	0.0258
0.004	3.4043	0.0241	2.1983	0.0279
0.005	3.3495	0.0216	2.1817	0.0127
0.008	3.2194	0.0393	2.0487	0.0158
0.007	3.1409	0.0287	1.8493	0.0087
0.008	2.9017	0.0180	1.7934	0.0073

T_1 - spin-lattice relaxation time; T_2 - spin-spin relaxation time

TABLE 5.19

Relaxation Times (T_1 and T_2) for aqueous solutions of sodium di-hydrogen phosphate at 363 K.

Mole fraction X	T_1 sec	Error	T_2 sec	Error
Water	3.6023	0.0324	2.8230	0.0581
0.001	3.2091	0.0126	2.4710	0.0259
0.003	2.5002	0.0159	1.4717	0.0259
0.005	1.9775	0.0098	1.1354	0.0181
0.007	1.6601	0.0155	0.9456	0.0130
0.009	1.3574	0.0147	0.8289	0.0141
0.011	1.1930	0.0153	0.7083	0.0157
0.013	1.0337	0.0123	0.6289	0.0180
0.015	0.9641	0.0094	0.6159	0.0145
0.017	0.9255	0.0083	0.6089	0.0268
0.019	0.8008	0.0098	0.5516	0.0173
0.021	0.7006	0.0127	0.4761	0.0119
0.025	0.5694	0.0085	0.2555	0.0135
0.030	0.4917	0.0044	0.3925	0.0180

T_1 - spin-lattice relaxation time; T_2 - spin-spin relaxation time

TABLE 5.20

Relaxation Times (T_1 and T_2) for aqueous solutions of potassium di-hydrogen phosphate at 303 K.

Mole fraction X	T_1 sec	Error	T_2 sec	Error
Water	3.8023	0.0324	2.8230	0.0581
0.001	3.5163	0.0242	3.4500	0.0252
0.003	3.4353	0.0380	3.2960	0.0677
0.005	3.1818	0.0130	3.0640	0.0101
0.007	2.9281	0.0121	2.8170	0.0189
0.009	2.7382	0.0124	2.6608	0.0251
0.011	2.5089	0.0095	2.2760	0.0172
0.013	2.3408	0.0082	2.0945	0.0184
0.015	2.2338	0.0135	2.0700	0.0190
0.017	2.1735	0.0192	2.1580	0.0228
0.019	2.1488	0.0144	2.0892	0.0273
0.021	2.0115	0.0104	1.9932	0.0303
0.025	1.8500	0.0114	1.8441	0.0225
0.030	1.6127	0.0123	1.6010	0.0114

T_1 - spin-lattice relaxation time; T_2 - spin-spin relaxation time

TABLE 5.21

Ultrasonic absorption and related parameters in aqueous solutions of ammonium chloride at 303 K.

Mole fraction X	Kgm^{-3} ρ	ms^{-1} C	10^{-15} $(\alpha/f^2)_{\text{obs}}$	$\text{Np m}^{-1} \text{s}^2$ $(\alpha/f^2)_{\text{cl}}$	10^{-3} $(\alpha/f^2)_{\text{ex}}$	Nsm^{-2} η_v	10^{-11} sec τ
Water	995.65	1510.00	22.58	6.12	16.46	2.86	17.29
0.01	1007.21	1531.27	22.50	5.70	16.80	3.08	18.19
0.02	1013.10	1547.62	21.83	5.55	16.28	3.11	18.36
0.03	1019.48	1575.08	21.15	5.15	16.00	3.24	18.87
0.04	1023.50	1590.05	21.07	5.02	16.05	3.36	19.42
0.05	1031.58	1606.57	19.97	4.83	15.14	3.29	19.13
0.06	1037.93	1622.06	17.62	4.72	12.90	2.91	17.51
0.07	1043.64	1639.09	14.80	4.58	10.22	2.39	15.24
0.08	1047.33	1650.97	13.60	4.47	9.13	2.19	14.36

X - concentration of ammonium chloride in mole fraction;

ρ - density of the solution;

C - ultrasonic velocity;

$(\alpha/f^2)_{\text{obs}}$ - observed absorption;

$(\alpha/f^2)_{\text{cl}}$ - classical absorption;

$(\alpha/f^2)_{\text{ex}}$ - excess absorption;

η_v - volume viscosity;

τ - structural relaxation time

TABLE 5.22

Ultrasonic absorption and related parameters in aqueous solutions of ammonium di-hydrogen phosphate at 303 K.

Mole fraction X	Kg m^{-3}	ms^{-1}	$10^{-15} \text{ Np m}^{-1} \text{ s}^2$			10^{-3} Nsm^{-2}	10^{-11} sec
	ρ	C	$(\alpha/f^2)_{\text{obs}}$	$(\alpha/f^2)_{\text{cl}}$	$(\alpha/f^2)_{\text{ex}}$	η_v	τ
Water	995.85	1510.00	22.58	6.12	16.46	2.86	17.29
0.01	1036.94	1565.53	26.04	6.16	19.88	4.02	23.20
0.02	1081.89	1601.97	21.52	6.54	14.98	3.33	21.08
0.03	1090.11	1633.36	20.90	7.03	13.87	3.35	22.24
0.04	1116.84	1665.54	17.02	7.61	9.41	2.47	19.68
0.05	1144.76	1700.40	15.43	8.16	7.27	2.08	19.45
0.06	1168.52	1714.26	12.60	9.12	3.48	1.04	16.62
0.07	1187.24	1716.65	10.62	10.22	0.40	1.21	19.09

X - concentration of ammonium di-hydrogen phosphate in mole fraction;

ρ - density of the solution;

C - ultrasonic velocity;

$(\alpha/f^2)_{\text{obs}}$ - observed absorption;

$(\alpha/f^2)_{\text{cl}}$ - classical absorption;

$(\alpha/f^2)_{\text{ex}}$ - excess absorption;

η_v - volume viscosity;

τ - structural relaxation time

TABLE 5.23

Ultrasonic absorption and related parameters in aqueous solutions of ammonium oxalate at 303 K.

Mole fraction X	Kgm ⁻³ ρ	ms ⁻¹ C	10 ⁻¹⁵ Np m ⁻¹ s ²			10 ⁻³ Nsm ⁻² η _v	10 ⁻¹¹ sec τ
			(α/f ²) _{obs}	(α/f ²) _{cl}	(α/f ²) _{ex}		
Water	995.65	1510.00	22.58	6.12	16.46	2.86	17.29
0.001	998.61	1519.27	23.37	6.04	17.33	3.09	18.35
0.002	1000.98	1528.23	20.92	5.99	14.93	2.71	16.73
0.003	1004.54	1531.45	19.40	6.00	13.40	2.46	15.69
0.004	1008.39	1541.39	18.10	5.97	12.13	2.28	14.98
0.005	1011.06	1549.71	17.00	5.89	11.11	2.13	14.35
0.006	1014.32	1552.89	15.13	5.93	9.20	1.78	12.89
0.007	1016.69	1563.97	13.82	5.88	7.94	1.57	12.04
0.008	1019.65	1569.82	12.61	5.90	6.71	1.35	11.16

X - concentration of ammonium oxalate in mole fraction;

ρ - density of the solution;

C - ultrasonic velocity;

(α/f²)_{obs} - observed absorption;

(α/f²)_{cl} - classical absorption;

(α/f²)_{ex} - excess absorption;

η_v - volume viscosity;

τ - structural relaxation time

TABLE 5.24

Ultrasonic absorption and related parameters in aqueous solutions of sodium di-hydrogen phosphate at 303 K.

Mole fraction X	Kgm ⁻³ ρ	ms ⁻¹ C	10 ⁻¹⁵ Np m ⁻¹ s ²			10 ⁻³ Nsm ⁻²	10 ⁻¹¹ sec
			(α/f ²) _{obs}	(α/f ²) _{cl}	(α/f ²) _{ex}	η _v	τ
Water	995.85	1510.00	22.58	6.12	16.46	2.86	17.29
0.001	1009.33	1517.37	23.47	6.30	17.17	3.07	18.49
0.003	1019.59	1529.45	22.06	6.39	15.67	2.89	17.93
0.005	1028.60	1544.15	20.76	6.36	14.40	2.76	17.54
0.007	1038.40	1557.21	19.56	6.36	13.20	2.62	17.11
0.009	1047.44	1568.00	18.56	6.51	12.05	2.46	16.70
0.011	1055.99	1571.32	16.56	6.57	9.99	2.09	15.26
0.013	1064.29	1579.23	14.53	6.82	7.71	1.64	13.60
0.015	1073.08	1590.04	13.90	6.83	7.07	1.55	13.40
0.017	1082.37	1597.50	14.68	6.97	7.71	1.72	14.44
0.019	1090.92	1605.71	15.35	7.13	8.22	1.88	15.46
0.021	1099.22	1617.75	16.00	7.14	8.86	2.09	16.63
0.025	1118.00	1640.00	16.77	7.19	9.58	2.39	18.43
0.030	1136.60	1649.62	17.24	7.16	10.08	2.61	19.65

X - concentration of sodium di-hydrogen phosphate in mole fraction;

ρ - density of the solution;

C - ultrasonic velocity;

(α/f²)_{obs} - observed absorption;

(α/f²)_{cl} - classical absorption;

(α/f²)_{ex} - excess absorption;

η_v - volume viscosity;

τ - structural relaxation time

TABLE 5.25

Ultrasonic absorption and related parameters in aqueous solutions of potassium di-hydrogen phosphate at 303 K.

Mole fraction X	Kgm ⁻³ ρ	ms ⁻¹ C	10 ⁻¹⁵ Np m ⁻¹ s ²			10 ⁻³ Nsm ⁻² η _V	10 ⁻¹¹ sec τ
			(α/f ²) _{obs}	(α/f ²) _{cl}	(α/f ²) _{ex}		
Water	995.65	1510.00	22.58	6.12	16.46	2.73	16.79
0.001	1000.05	1512.92	21.73	6.16	15.57	2.73	16.79
0.003	1010.80	1523.66	21.19	6.14	15.05	2.73	16.92
0.005	1020.57	1532.00	20.63	6.18	14.45	2.69	16.91
0.007	1031.08	1541.97	18.72	6.18	12.54	2.40	15.79
0.009	1040.85	1555.85	18.03	6.14	11.89	2.36	15.77
0.011	1051.11	1565.19	15.83	6.43	9.40	1.92	14.24
0.013	1060.15	1575.71	14.13	6.46	7.67	1.62	13.12
0.015	1070.42	1586.42	13.01	6.44	6.57	1.42	12.40
0.017	1079.70	1593.36	12.63	6.55	6.08	1.35	12.33
0.019	1087.76	1603.93	13.20	6.53	6.67	1.52	13.23
0.021	1098.03	1611.30	13.72	6.59	7.13	1.66	14.06
0.025	1117.77	1629.00	14.84	6.59	8.25	2.02	16.00
0.030	1134.43	1641.49	15.30	6.61	8.69	2.21	17.14

X-concentration of potassium di-hydrogen phosphate in mole fraction;

ρ - density of the solution;

C - ultrasonic velocity;

(α/f²)_{obs} - observed absorption;

(α/f²)_{cl} - classical absorption;

(α/f²)_{ex} - excess absorption;

η_V - volume viscosity;

τ - structural relaxation time

REFERENCES

1. S. Barnartt
Quart. Revs., 7, 84, (1953).
2. L. Bergmann
"Der. Ultraschall", 6th Ed., P336-341, 427-428, Hirzel,
Stuttgart (1954b).
3. H. Harned and B. Owen
"The Physical Chemistry of Electrolytic solutions",
P 356-370, Reinhold, New York (1958b).
4. C. Balachandran
J. Indian Inst. Sci., 38 A, 1 (1958a).
5. P. Padmini and B. Rao
Ind. J. Phys., 34, 565 (1980).
6. D. Ailam and W. Lee
Nature, 191, 1388 (1981).
7. K. Ramabrahman
Ind. J. Pure & Appl. Phys., 6, 75 (1968).
8. D. Anbananthan, B. Krishnan and A. Srinivasa Rao
Ind. J. Chem., 14A, 277 (1975).
9. T.K. Nambinarayanan and A. Srinivasa Rao
Ind. J. Pure & Appl. Physics, 16, 711 (1978).
10. M.J. Blandamer
"Introduction to Chemical Ultrasonics", Academic Press,
London (1973).
11. J. Kavanau
"Water and Solute-Water Interactions", Holden Day
Inc., Amsterdam (1984).
12. A. Juszkiewicz and F. Figlerowicz
Ultrasonics, 28, 391 (1990).
13. C. Muralikrishna, Ramachandra Reddy, N. Prabhahara Rao and
K.C. Reddy, Pramana, 13, 105 (1979).
14. H.S. Frank and W.Y. Wen
Discuss. Faraday. Soc., 24, 133 (1957)
15. A. Srinivasa Rao, A. Sundaramoorthy and V. Arulmozhi
J. Mol. Liq., 45, 231 (1990).
16. A. Srinivasa Rao, R. Srinivasan and V. Arulmozhi
Ind. J. Pure & Appl. Phys., 29, 588 (1991).
17. S. Rajalakshmi
M. Phil Thesis, Pondicherry University (1988).

18. V. Arulmozhi,
"NMR relaxation studies in biological tissues and on structural aspects of some solutions", Ph.D Thesis, Pondicherry University (1991).
19. G. Kurtze and K. Tamm
Acustica, 3, 33 (1953).
20. O. Wilson and R. Leonard
J. Acoust. Soc. Am., 26, 223 (1954).
21. K. Tamm and H. Haddenhorst
Acustica, 4, 853 (1954).
22. K. Tamm, G. Kurtze and R. Kaiser
Acustica, 4, 380 (1954).
23. R. Barret and R. Beyer
Phys. Rev., 84, 1060 (1951).
24. R. Barret, R. Beyer and F. Mc Namara
J. Acoust. Soc. Am., 26, 966 (1954).
25. J.R. Pellam and J.K. Galt
J. Chem. Phys., 14, 808 (1946).
26. J.M.M. Pinkerton
Nature, 160, 128 (1947).
27. H. Ratajczak and W.J.Orville Thomas
"Molecular Interactions", Vol.3, John-Wiley & Sons, New York (1982).
28. H.Endo and O. Nomoto
J. Chem. Soc. Faraday Trans.2, 77, 217 (1981).
29. L. Hall
Phys. Rev., 73, 775 (1948).
30. W.P. Mason
"Physical Acoustics", Vol.II, Part A, Academic Press, London (1965).