

PART I

**EFFECT OF ELECTROLYTES ON
THE TEMPERATURE OF SOUND
VELOCITY MAXIMUM IN
WATER**

CHAPTER 1

INTRODUCTION

1.1 Review of the previous experimental work on the effect of electrolytes on the temperature of sound velocity maximum of water

Water is distinct from other liquids as it exhibits density maximum at 3.98°C, heat capacity minimum at 35°C, adiabatic compressibility minimum at 64°C, specific acoustic impedance maximum at 56.4°C and sound velocity maximum at 74°C. This peculiar behaviour of water has been attributed to its structure. At any given temperature there exists an equilibrium between hydrogen bonded clusters (voluminous, open packed and ice like structure) and non-hydrogen bonded monomers (close packed and dense structure) of water. Increase in temperature leads to the rupture of the hydrogen bonded clusters giving rise to monomers. The extrema exhibited by water in its physical properties at different temperatures can be explained on the basis of the change in the hydrogen bonded structure of water.

The presence of a solute (either electrolyte or non-electrolyte) in water affects the structural equilibrium as a result of any one of the phenomena taking place, like stabilization of the hydrogen bonded clusters against thermal collapse, promotion of long range order, formation of clathrate hydrate like structures or collapse of the hydrogen bonded clusters. This in turn leads to a shift in the temperature at which the extrema in the physical properties of water have been observed.

According to Eyring and Kincoïd [1,2] a sound wave in a liquid travels with infinite velocity within a molecule and with gas kinetic velocity in the intermolecular space. Rise in the temperature of pure water leads to structural breakdown. The population of close packed structures increases leading to a positive temperature

coefficient of sound velocity. Simultaneously, there occurs an increase in the mean distance between the molecules due to rise in temperature which results into a negative temperature coefficient of sound velocity. The observed sound velocity maximum at 74°C can be thought of as arising out of these two opposing tendencies. Beyond 74°C, the structural expansion plays a dominant role and the sound velocity decreases with temperature.

Any parameter which can affect the structural equilibrium will also influence the temperature of sound velocity maximum (TSVM) of water. In aqueous electrolytic solutions, there exist ion-ion, ion-solvent and solvent-solvent interactions. Hence ultrasonic velocity measurements in aqueous electrolytic solutions in the near vicinity of TSVM will help in delineating the structural effects of different ions. A brief review of the work carried out by different researchers on the effect of electrolytes on TSVM of water is presented below.

Tamm and Haddenhorst [3] measured ultrasonic velocities in aqueous solutions of magnesium sulphate at different temperatures in the range 15 to 60°C by forming Hiedemann fringes. The temperature dependence of ultrasonic velocity has been determined by observing the periodically occurring 'temperature resonances' in a stationary ultrasonic wave. The dependence of ultrasonic velocity on temperature was found to be parabolic as in water and the maximum shifted to lower temperatures. The authors explained the results on the assumption of disintegrations of aggregates of water molecules. The measurements were made at intervals of 5°C and only rising portions of the curves were studied. The TSVM values were evaluated by

extrapolation of the $\left(\frac{du}{dt}\right)$ versus temperature (t) plot to zero values of $\left(\frac{du}{dt}\right)$. This type of procedure involving extrapolation of the measurements, far beyond the range of measurements, yields values of TSVM with large uncertainties. The accuracy in fixing TSVM is $\pm 3^\circ\text{C}$.

Mikhailov [4-8] and his co-workers studied the ultrasonic behaviour of aqueous solutions of a large number of electrolytes covering the temperature range on either side of TSVM. The accuracy in sound velocity measurement is ± 0.05 per cent. In general TSVM was found to decrease with concentration of the electrolyte. However in the case of LiOH an increase in TSVM was observed up to 0.5 m and a decrease thereafter. The accuracy in fixing TSVM in these studies is estimated to be around $\pm 2^\circ\text{C}$.

Marks [9,10] determined ultrasonic velocities in aqueous solutions of Li_2SO_4 , Na_2SO_4 , K_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, MgSO_4 , LiOH , NaOH , KOH and NH_4OH in the temperature range $0-80^\circ\text{C}$ covering the concentration range $0-5$ m. The temperatures of sound velocity maximum (TSVM) of electrolyte solutions were determined using the template of the curve of ultrasonic velocity versus temperature of pure water and taking the maximum value as that corresponding to the maximum point on the template for concentrations up to 1.0 m. For higher concentrations the curves are flat and the maximum was determined from the smoothed curves. The accuracy in fixing TSVM, according to Marks, is around ± 2 to 5°C when the velocity measurements are accurate to only ± 0.1 to ± 0.2 per cent. This is particularly true at higher concentrations. The results of Marks do not show positive shift of TSVM in the case

of LiOH. For example, at a concentration of 0.24 m, the value of TSVM is 72°C while the results of Mikhailov show a value of 75°C at 0.237 m. Apparently there is disagreement between the two values. However, if we consider the uncertainty of $\pm 2^\circ\text{C}$ in the determination of TSVM, the results of Mikhailov and Marks agree with each other.

Subrahmanyam and Sivakumar [11] who could estimate TSVM with an accuracy $\pm 0.2^\circ\text{C}$ observed a positive shift in TSVM of aqueous LiOH at low concentrations indicating LiOH as a structure promoter.

Pancholy and Singal [12] studied the temperature variation of ultrasonic velocity in the range 15 - 68°C in aqueous solutions of sodium formate, sodium acetate, sodium propionate, sodium isovalerate, calcium formate, calcium acetate, calcium propionate, lead acetate, zinc acetate and barium acetate using a pulse technique working at 20 MHz. The results indicate a decrease of TSVM with increasing concentration. However, the authors could not fix up TSVM precisely due to the flatness of the curves.

Gnanamba and Ramachandra Rao [13] studied the temperature variation of ultrasonic velocity in aqueous solutions of ZnSO_4 , $\text{Cr}_2(\text{SO}_4)_3$, CdSO_4 , $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$, CoSO_4 and NiSO_4 over the temperature range 20-80°C at intervals of 10°C using a fixed path interferometer. It has been observed that the sound velocity versus temperature curves are similar to that for pure water and the TSVM is found to be displaced towards low temperatures with increasing concentration. The accuracy in

sound velocity measurements is ± 0.07 per cent. The accuracy in fixing TSVM is $\pm 2^\circ\text{C}$.

Nomoto and Endo [14,15] using an acoustic interferometer working at 5 MHz measured sound velocities in aqueous solutions of ammonium halides, ammonium sulphate and lead nitrate in the temperature range 20-100°C. The accuracy in velocity determination is ± 0.1 per cent and the measurements were made at intervals of 5°C. The accuracy in fixing TSVM is $\pm 3^\circ\text{C}$. It has been observed that the sound velocity versus temperature curves are parabolic in shape, similar to that in pure water, but displaced to lower temperatures with increase in the concentration. The results on aqueous solutions of $(\text{NH}_4)_2\text{SO}_4$ and $\text{Pb}(\text{NO}_3)_2$ indicate a decrease of TSVM with increasing concentrations. However, the TSVM remains constant (74°C) up to 5 mole per cent for ammonium halides. The shift in TSVM becomes positive above 5 mole per cent in the case of ammonium chloride. Above 5 mole per cent, the TSVM remains the same (74°C) for solutions of ammonium bromide in the entire concentration range studied, while the TSVM is found to decreased with increasing concentration in the case of ammonium iodide.

Subrahmanyam and Raghavan [16] measured ultrasonic velocities with an accuracy of $\pm 0.003\%$ in aqueous solutions of LiCl, LiBr, LiI, NaCl, KCl and RbCl in the temperature range 66-80°C using variable path interferometer working at 3 MHz. The ultrasonic velocity measurements were made at intervals of 2 to 3°C. The change in TSVM of water due to addition of electrolytes was evaluated with an accuracy of $\pm 0.2^\circ\text{C}$. The authors reported an increase of TSVM in the case of lithium

chloride and lithium bromide with increase in concentration (positive shift) up to concentrations 0.8 m and 0.3 m respectively and a decrease thereafter. For rest of the alkali halides studied, the TSVM decreases with increasing concentration. These authors have estimated the structural contribution to the shift in TSVM after accounting for dilution effect and the results were discussed in the light of the structure making and structure breaking nature of the ions studied.

Sivakumar [17] studied the effect of alkali halides (LiF, NaF, KF, NaI and KI), alkali nitrates (LiNO₃, NaNO₃ and KNO₃), alkali acetates and formates on TSVM of pure water and evaluated the structural contribution to the shift in TSVM by accounting for the dilution effect. The results are explained in the light of structure making and structure breaking nature of the anions and cations.

Achari [18] *et al.* studied the effect of lithium carbonate, ammonium phosphate, ammonium acetate and strontium acetate on TSVM of water by measuring ultrasonic velocities in aqueous solutions of these electrolytes in the temperature range 50 to 80°C. The shift in the TSVM of water is found to be positive for ammonium phosphate reaching maximum around 0.07 m and thereafter decreasing indicating that at higher concentrations, the conditions are not favourable for stabilization of water structure. At low concentrations ammonium phosphate behaves as a structure promoter. The shift in TSVM of water is found to be negative throughout the concentration range studied (0.12 m) indicating the structure breaking nature of these electrolytes.

The effect of non-electrolytes on the temperature of sound velocity maximum of water have been studied extensively [19-35] and the studies have been found to be highly useful in classifying the solutes as structure makers and structure breakers.

The presence of small amounts of a non-electrolyte in an aqueous electrolyte solution is found to affect the ion-ion and ion-solvent interactions leading to a change in the hydrogen bonded structure of water. Apart from other physico-chemical studies [36-50] TSVM studies have been found to be useful in understanding the ion-solvent interactions in the presence of a non-electrolyte in aqueous solutions.

Manohara Murthy and Subrahmanyam [51] studied the effect of NaCl, KCl, RbCl, KBr and KI on the temperature of sound velocity maximum (TSVM) of aqueous t-butanol. The structural contribution to the shift in the TSVM of aqueous t-butanol by the addition of alkali halides was found to be in the order NaCl > KCl > RbCl and KCl > KBr > KI thereby indicating the $\text{Na}^+ > \text{K}^+ > \text{Rb}^+$ and $\text{Cl}^- > \text{Br}^- > \text{I}^-$ in disrupting the hydrogen bonded structure of water. However the order is the reverse of that found for pure water i.e., $\text{Rb}^+ > \text{K}^+ > \text{Na}^+$ and $\text{I}^- > \text{Br}^- > \text{Cl}^-$. The results have been explained on the basis of hydrophobic - hydrophilic interactions prevalent in the ternary systems.

Seshappa *et al.* [52,53] studied the effect of alkali halides on the TSVM of aqueous solutions of formamide, dimethyl sulphoxide, N-methyl formamide and N,N-dimethylformamide and found enhancement in the structure breaking nature of anions and cations.

The brief review presented above indicates the usefulness of sound velocity measurements in the vicinity of maximum sound velocity temperature in aqueous

solutions of electrolytes in understanding the ion-ion, ion-solvent and solvent-solvent interactions. Sound velocity measurements have to be made with higher degree of accuracy to fix up precisely the TSVM of the solution and dilution effect has to be taken into account to delineate the structural contribution to the shift in TSVM of water and from this angle the studies made are not extensive.

In the present work the effect of sulphates of lithium, sodium, potassium, magnesium and ammonium, chlorides of magnesium, calcium, strontium and barium and ammonium halides on TSVM of water have been studied.

Literature survey also indicates that only the effect of single electrolytes on the temperature of sound velocity maximum have been studied. It will be interesting to see how the structural interactions would be in the presence of a third ion and in this direction the author has taken up the studies on the effect of mixed electrolytes on TSVM of water. The mixed electrolytes chosen for study are (NaCl + KCl), (NaBr + KBr), (NaI + KI), (NaCl + NaBr), (NaBr + NaI), (NaCl + NaI), (KCl + KBr), (KBr + KI) and (KCl + KI).

It is necessary to have a thorough knowledge of the structural peculiarities of water to understand the ion-ion, ion-solvent and solvent-solvent interactions in aqueous electrolyte solutions. In view of this a detailed account of the various models proposed for the structure of water is presented in Section 1.2.

1.2 Structure of liquid water

The anomalous behaviour of water in many of its physical properties such as density, ultrasonic velocity, heat capacity, adiabatic and isothermal compressibilities heat capacity etc. as function of temperature and the peculiarities observed in dilute aqueous electrolyte solutions are mainly due to the structure of water. In view of this, it is essential to have a thorough knowledge of the structural peculiarities of water. Hence a brief review of the various models proposed for the structure of water is presented below.

In recent years, many review articles and books, dealing extensively and critically on the structure of water have been published [54-62]. The spectroscopic model of water is shown in Fig. 1.2.1. It is a bent molecule. The angle between the two hydrogens is 105° . The structure of water molecule can be understood in terms of Sp^3 hybridization of the oxygen orbitals. Of the four Sp^3 hybrid orbitals of oxygen, two contained paired electrons of opposite spin and the other two contain unpaired electrons. The two orbitals containing unpaired electrons overlap with the $1s$ orbitals of the two hydrogen atoms forming bonds. The observed angle is less than the tetrahedral angle ($109^\circ 28'$). This is due to the repulsions exerted by the lone-pair of electrons on the bonding electrons. The large dipolemoment of water molecule is due to the bent structure of water molecule with an excess of negative charge on the oxygen end of the molecule and an equal excess of positive charge on the hydrogen end. The electrons of the covalent bonds are thus pushed close to the oxygen atoms, leaving the hydrogen atoms as almost bare protons. This results in an attraction

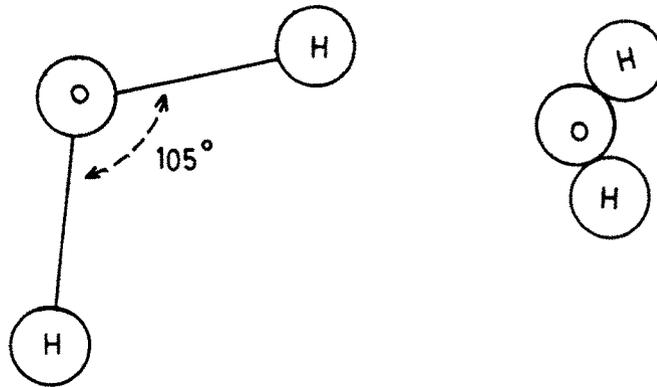


Fig. 1.2.1 Model of water molecule.

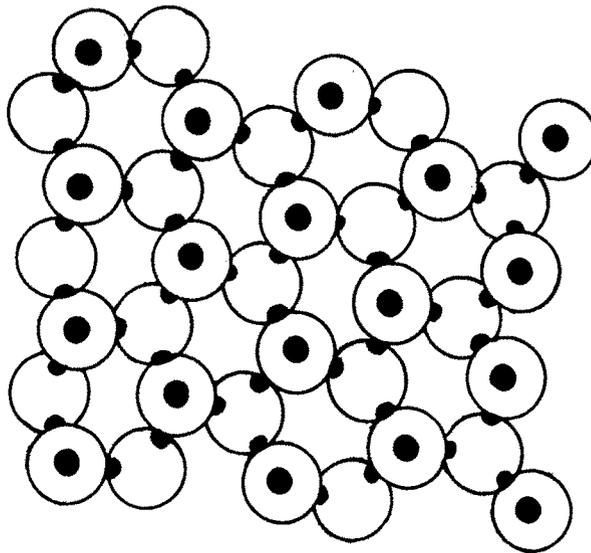


Fig. 1.2.2 Model of ice structure

Solid dots represent hydrogen atoms
Circles represent oxygen atoms.

between the negative oxygen end of one molecule and the positive end of another. This attraction is stronger than simple attraction between dipoles and is named as hydrogen bond.

The various models proposed to predict the bulk structure of water may be classified into continuum models [63-67] and mixture models [68-77]. The continuum models treat liquid water as a uniform dielectric medium. When averaged over a large number of molecules, the environment of each molecule looks the same as that of any other and hence the behaviour of all molecules is equivalent. A continuum theory of liquid water sees the structure as showing single distribution of oxygen-oxygen distances, oxygen-oxygen-oxygen angles and energies. The average bond energy changes with temperature and pressure because of changes in the distribution of bond lengths and of distortion angles. The continuum model may also be called as 'tetrahedral network model.' Based on this model, the breaking of ice lattice on melting can be explained as due to the loss of long range order with rise in temperature owing to distortion of the oxygen-oxygen-oxygen angles and oxygen-oxygen distances while preserving tetrahedral coordination at the typical oxygen atom.

The mixture models consider water as a mixture of two or more distinguishable species in chemical equilibrium. Many mixture models assume that one of the species is ice-like. Hence, there is a need to consider the structure of ice [78]

The basic structural details of the hydrogen-bonded solid water (ice) are shown in Fig. 1.2.2. Each oxygen atom is surrounded by its two covalently bonded hydrogen atoms and two additional hydrogen atoms held by hydrogen bonds. Thus ice is a giant polymeric molecule held together by hydrogen-bonds with four hydrogen atoms spaced tetrahedrally about each oxygen atom. The structure is open and honey-combed with hexagonally shaped channels which make ice relatively less dense. The oxygen atoms in ice are also tetrahedrally coordinated to three others in the same layer and one other in an adjacent layer. The tetrahedral structure is body-centred cubic with the reference molecule surrounded by four other molecules situated at alternate corners of the cube as shown in Fig. 1.2.3. The data of radial distribution curves obtained from X-ray diffraction by Narten and Levy [79] indicate that the number of nearest neighbours is approximately 4.4. Thus the coordination number is slightly greater than 4 which indicates that some of the vacant cube corners might be occupied by molecules which are not hydrogen-bonded to the central molecules, considered from the stand point of the reference molecule, a total of nine molecular species may be obtained by successive breaking of hydrogen-bonds. These species differ in terms of both the number of molecules that are hydrogen-bonded to the reference molecule and the bonds involved. The mixture models [80-84] proposed, assume the existence of two states, one consisting of tetrahedrally coordinated ice-like structure and the other consisting of a close-packed monomers.

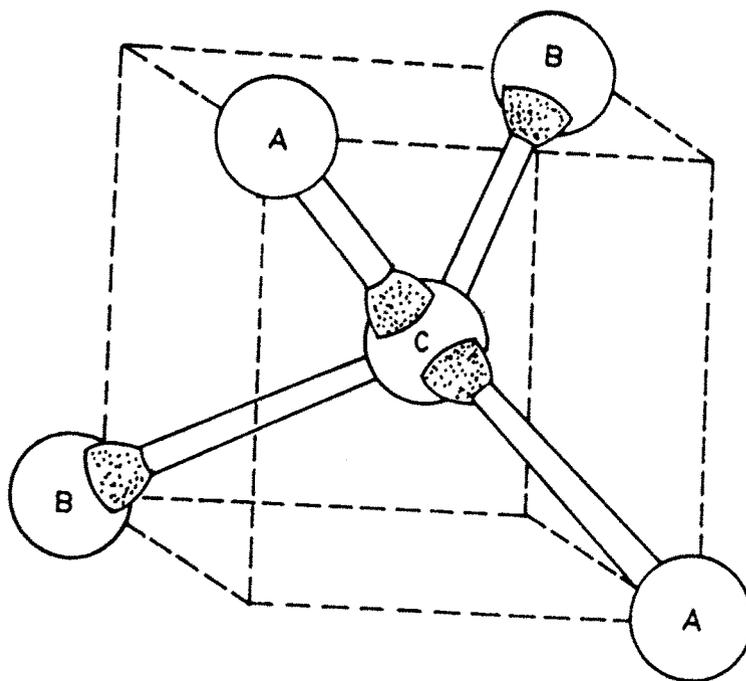


Fig. 1.2.3 Tetrahedral arrangement of nearest neighbours in ice. Hydrogen atoms are shaded. The relation of tetrahedral structure to a body-centred-cubic structure is indicated. The nearest neighbours of the reference molecule (C) are of two types; those connected through one of the hydrogen atoms belonging to the reference molecule (A), and those connected through one of the lone electron pairs of the reference molecule (B).

Based on a study of the diffraction of X-rays by liquid water, Bernal and Fowler [63] assumed liquid water to consist of a mixture of single water molecules which are free of hydrogen-bonds and clusters of molecules held together by hydrogen-bonds as in ice. The hexagonal channels may also be filled with some of the monomers. The fact that the density of water is maximum at 3.98°C can be attributed to the two opposing effects, namely, the increase in volume resulting from the thermal expansion and the decrease in volume resulting from the breakdown of hydrogen-bonded clusters. Above 3.98°C the thermal expansion plays a dominant role and the density steadily decreases with rise in temperature. This model is primarily qualitative in nature and did not yield a partition function or thermodynamic parameters.

Lennard-Jones and Pople [64] considered water as an irregular arrangement of H₂O molecules with bent hydrogen-bonds. Pauling [70] considered that the hydrate structures like Cl₂8H₂O and CH₄6H₂O represent the hydrogen-bonded structures present in liquid water. Though Pauling's model was criticized as too rigid a model, it predicts correct density.

Wada [84] proposed a simplified model for the structure of water. According to this model, water is considered as an equilibrium mixture of open-packed and close-packed structures. The molar volumes of these two types of structures are assumed to be linear functions of temperature. This model also explains the fact that the number of first neighbours increases with temperature [85]. The Self-diffusion, ionization and electrical conductivity of water were explained based on this model.

The effect of non-electrolytes on the temperature of density maximum of water was discussed by Wada and Umeda [86,87] using this model.

Frank and Wen [68,88] proposed the 'flickering cluster' model. According to this model, each oxygen atom can form four approximately tetrahedrally disposed hydrogen-bonds. The formation of the bonds is considered to be essentially a cooperative process. Thus when a favourable energy fluctuation promotes the formation of a bond, many are formed simultaneously, a self-stabilizing three dimensional hydrogen bonded cluster jumps into existence and persists until it suffers a collective destruction by an unfavourable energy fluctuation. The single dielectric relaxation time of water (10^{-11} s) is taken as indicative of the short life of the clusters.

Frank and Quist [89] proposed a two-state model of water based on the structure of water suggested by Pauling [70]. According to Pauling, liquid water has a structure similar to gas hydrates, known as clathrates. The liquid water is regarded as 'water hydrate' consisting of a frame work similar to that found in the gas hydrate with the voids filled by single water molecules. Accordingly, the two states are frame work water consisting of species which are hydrogen-bonded and interstitial water consisting of species that are non-hydrogen-bonded. The calculations of Frank and Quist contain several unique features. They have taken into account the interaction between molecules in different states and a combinational factor, which defines the number of ways in which the monomers can be distributed among sites. The validity of this approach for liquid water is questionable since it is difficult to reconcile the concept of frame work structure that is sufficiently static to provide sites fixed in

space with the concept of 'flickering clusters' of varying extent continuously forming and breaking up. Relaxation parameters obtained by using this model are found to be small.

Nemethy and Scheraga [54] proposed a five state model for the structure of water in line with the ideas proposed by Frank and Wen [68,88]. Nemethy and Scheraga assumed that the cooperative character of hydrogen-bonding results in the formation and breakdown of clusters of hydrogen-bonded molecules. These clusters are short lived, forming and melting as a consequence of local energy fluctuations. These clusters are also considered to be imbedded in, and in equilibrium with monomeric unbonded water molecules. As per this model, eventhough liquid water consists of only two main structures namely the clusters and monomers, the molecules themselves are divided into five species of varying energy and internal freedom depending on the number of hydrogen-bonds in which they are participating. The interior of the clusters contain molecules with all four hydrogen-bonds unbroken, while on the surface of the clusters, molecules with three, two and one hydrogen-bonds can be found. The molecules occupying the space in between the clusters have all four bonds broken. Nemethy and Scheraga derived some thermodynamic parameters of pure water like free energy and enthalpy which are in good agreement with the experimental data. However, they could not explain the minimum in the heat capacity versus temperature curve at 35°C.

Samoilov [90] proposed the 'interstitial model.' This model was supported by Danford and Levy [91] on the basis of their X-ray diffraction studies. In this

'interstitial model,' the cavities of the hydrogen-bonded clusters are considered to be partially populated with non-hydrogen-bonded monomeric water molecules. This model, though suitable for water at low temperatures, is hardly appropriate over the whole temperature range within which water can exist as a liquid. This model is not consistent with the flexibility of hydrogen-bonds [55], not implicit in Frank and Wen's view of cluster formation [68,88] and finds no part in Nemethy and Scheraga's treatment [54] which also rejects the occupation of cavities by monomeric molecules.

Marchi and Eyring [92] proposed a model which visualizes the coexistence of free monomer water molecules and hydrogen-bonded ice-like clusters. The voids created due to the tetrahedral hydrogen-bonding in ice-like component can be occupied by freely rotating monomers. Rise in temperature increases the percentage of monomers which occupy the voids thereby reducing the total volume, but at the same time fluidised vacancies are being produced. Below 3.98°C the voids overshadow the introduction of vacancies. Above 3.98°C, water begins to behave as a normal liquid as far as the volume behaviour is concerned. Because of the increase in the concentration of the monomers with rising temperature, it will be necessary for the structure of the ice-like component to change to accommodate more rotating monomers. This would account for the various properties which reveal the structural changes and the minimum in the heat capacity versus temperature curve at 35°C. Using these concepts, besides significant structure theory, these authors have evaluated thermodynamic parameters such as Helmholtz free energy, entropy, molar volume and vapour pressure as a function of temperature in the range 0 to 200°C.

The calculated results agree reasonably well with the experimental results. This theory has been modified and improved by Mushik *et al.* [93] resulting in better agreement between theory and experiment.

In the theory proposed by Eucken [94-96] water is assumed to be an equilibrium mixture of octomers, quadrimers, dimers and monomers. Assuming the volume per mole of octomers would be 10% greater than that of others (quadrimers, dimers and monomers) in bulk water, Eucken proposed that water behaves normally even at 10000 atmospheres. He fitted an empirical equation of state to the high pressure data and extrapolated it to the atmospheric pressure. Smith and Lowson [82] questioned the validity of the assumption upon which this extrapolation is based, because they observed in their investigation of velocity of sound in water, anomalous behaviour to persist even at 10000 atmospheres.

Davis and Litovitz [74] proposed a model for liquid water based on the existence of puckered hexagonal rings, similar to these in ice, which are assumed to coexist in two structures; an open-packed ice-like structure and a close-packed structure. In the open-packed structures, hydrogen-bonds are formed between the puckered hexagonal rings, while in close-packed structures, the molecules occupy a nearly complete body-centred cubic structure. Based on this model the authors have explained the temperature variation of molar volume, heat capacity and other thermodynamic properties.

Eyring and co-workers [97] improved their earlier model and proposed a two-state model for water structure. According to this model, water consists of an

equilibrium mixture of clathrate-like clusters of approximately 45 molecules dispersed in an ice-III-like structure. The ice-I-like clusters exhibit the density of ice-I and are assumed to disappear at 4°C. The liquid is assumed to behave 'normally' above this temperature. The concept that water behaving anomalously only in the vicinity of 4°C is erroneous. Actually it is the temperature dependence of thermal expansion coefficient (α) that is anomalous and this anomaly extends over the entire temperature range. The variation of α with $\left(\frac{1}{VT^2}\right)$ where, V is the molar volume and T is the temperature in K is linear from 0°C to 100°C. Hence it is logical to assume that the structural mechanism responsible for density maximum at 4°C is still active even at 100°C.

The different models proposed, eventhough account for a number of distinctive features of liquid water, are contrary in many respects [55]. Eventhough the presence of a bulky four coordinated species has been universally accepted, the particular form of this species whether ice-like or similar to any form of cage or crystalline structure is still an open question. It is also not clearly established regarding the nature of the second species whether they are with no hydrogen-bonds (monomers) or with one, two or three hydrogen-bonds. Also, it is not well established whether monomers exist in the interstitial sites provided by hydrogen-bonded lattice or are dispersed among the clusters of the bulky hydrogen-bonded water molecules. It may be mentioned here that the very existence of second species itself is questioned by the proponents of continuum models of water.

To sum up the various models, the structural aspects of water common to many theories are as follows.

- i. Water is regarded as an equilibrium mixture of essentially two species - one a bulky ice-like structure with relatively low density (hydrogen-bonded) and the other a denser species formed by bending or breaking of hydrogen-bonds (non-hydrogen-bonded). The two species are shown schematically in Fig. 1.2.4.
- ii. At any temperature, there exists a dynamic equilibrium between the two types of species. The relative amounts of these species change continuously with temperature. Rise in temperature promotes the rupture of hydrogen-bonded clusters leading to an increase in the population of non-hydrogen-bonded dense component (monomers).

These aspects are utilized in the present study in explaining the ultrasonic behaviour of aqueous electrolyte solutions.

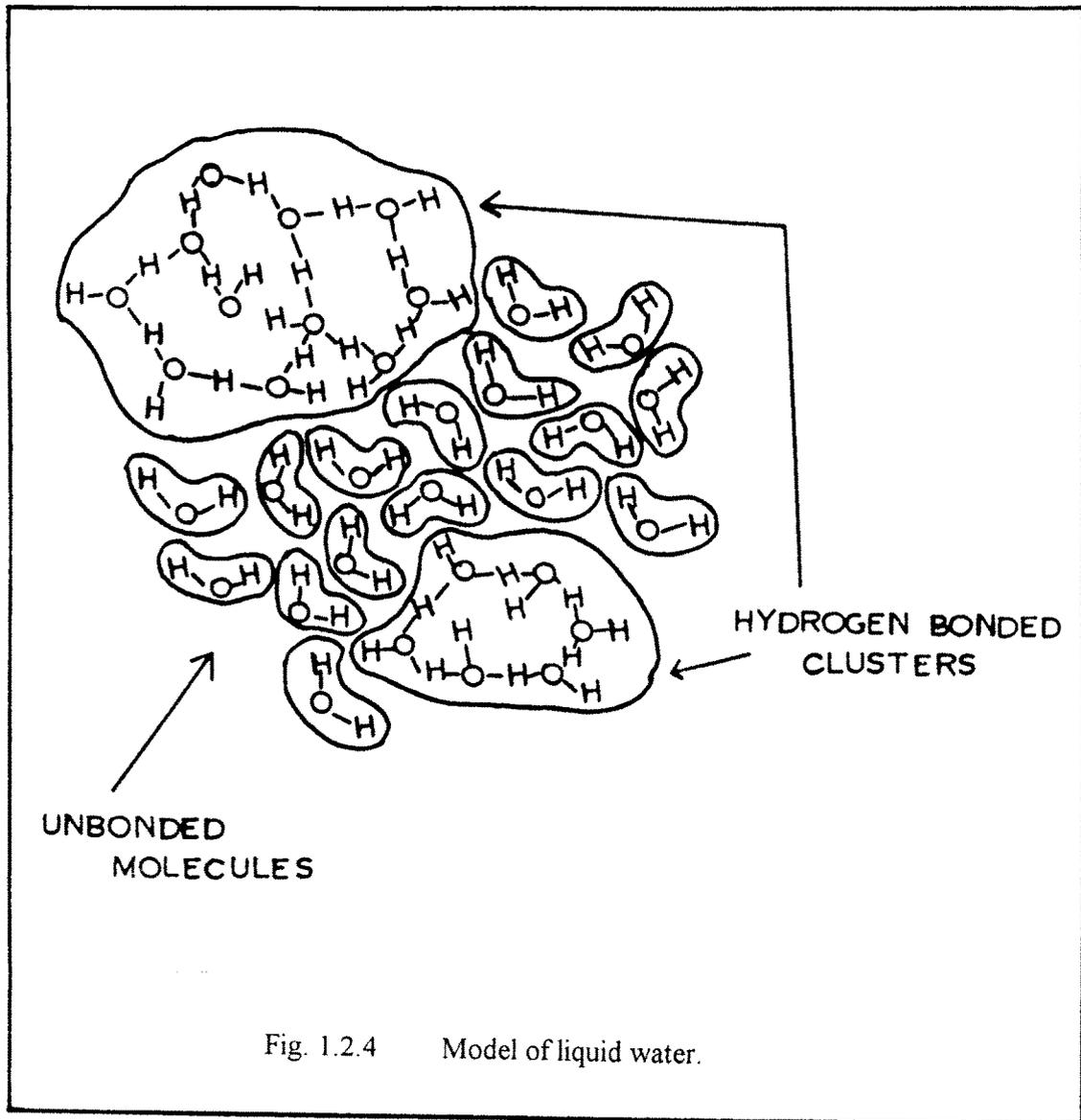


Fig. 1.2.4 Model of liquid water.