GENERAL SUMMARY

The programme of the work presented in this thesis deals with ultrasonic studies in aqueous solutions of electrolytes and nonelectrolytes. The thesis consists of two parts. Part I deals with the studies carriedout on the "Effect of electrolytes on the temperature of sound velocity maximum in water." Part II deals with "Ultrasonic studies on dilute solutions of water in nonelectrolytes."

Water is unique in showing a maximum in the sound velocity versus temperature relation at 74°C. This behaviour can be explained as due to the two opposing effects namely structural expansion and the shift in the equilibrium between the open-packed (hydrogen-bonded) and close-packed (non-hydrogen-bonded) structures in water. Any parameter which can affect the structural equilibrium will also influence the temperature of sound velocity maximum (TSVM). Chapters 1 to 5 of the thesis are devoted for the presentation of the studies concerning the effect of varies electrolytes on the temperature of sound velocity maximum in water.

A brief review of the previous experimental work on the effect of electrolytes on TSVM of water is presented in Section 1 of Chapter 1. To understand the nature of solute-solvent interactions responsible for the non-ideal behaviour, a knowledge of the structural peculiarities of water is essential. Hence, a brief review of the various theories concerning the structure of water is presented in Section 2 of Chapter 1.

Ultrasonic velocities in aqueous solutions of electrolytes were determined using a single crystal variable-path interferometer working at 3 MHz. The details of the experimental technique are presented in Chapter 2. The ultrasonic velocities evaluated from the wavelength measurements made near the source have to be corrected for diffraction effects. The method followed for effecting diffraction correction is also discussed in this chapter.

Results of measurements of ultrasonic velocity as a function of temperature in dilute aqueous solutions of Li_2SO_4, Na_2SO_4, K_2SO_4, $(NH_4)_2SO_4$, $MgSO_4$, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$, NH_4Cl, NH_4Br and NH_4I over a temperature range 64-80°C are presented in Chapter 3.

The shift in TSVM of water may be thought of as arising due to (a) dilution effect and (b) structural effect. The dilution effect is always negative (i.e., TSVM decreases with the addition of a solute) and the structural effect may be either positive or negative depending on the nature of the solute. For a comparative study of different solutes, it is necessary to separate out these two effects. The details of the method of evaluation of the ideal shift (dilution effect) are presented in Section 1 of Chapter 4. The structural contribution of the shift in TSVM of water, $[\Delta T_{str} = (T_s)_{exp} - (T_s)_{id}]$, has been evaluated for K_2SO_4, $(NH_4)_2SO_4$, NH_4Cl, NH_4Br and NH_4I in the present work. For the rest of solutes studied no attempt has been made to evaluate the ΔT_{str}, owing to the paucity of thermoelastic data at high temperatures.

The discussion on the results of the studies carriedout on the effect of sulphates of lithium, sodium, potassium, magnesium and ammonium on the temperature of sound velocity maximum of water is presented in Section 4.2. The velocity measurements were carriedout at $\simeq$ 2°C intervals over a range of 5°C on either side of TSVM of the solution. The shift in TSVM of water due to the addition of the electrolytes ΔT_{obs}, is found to be positive at low concentrations for Li_2SO_4 and $MgSO_4$ indicating Li^+ and Mg^{2+} as structure promoting ions. At higher concentrations ΔT_{obs} is negative for these solutes indicating the structure breaking nature at higher concentrations. ΔT_{obs} values for Na_2SO_4, K_2SO_4 and $(NH_4)_2SO_4$ are found to be negative throughout the concentration range studied. The structural contribution to the shift in TSVM of water, ΔT_{str}, for $(NH_4)_2 SO_4$ and K_2SO_4 are found to be negative indicating that these solutes behave as structure breakers. The results are explained in terms of the relative strengths of the structure making and breaking nature of anions and cations in the solution.

Section 4.3 deals with the effect of chlorides of magnesium, calcium, strontium and barium on the TSVM of water. ΔT_{obs} for $MgCl_2$ and $CaCl_2$ are positive at low concentrations becoming maximum around w $\simeq$ 2.3 x 10^{-2} for $MgCl_2$ and w $\simeq$ 1.9 x 10^{-2} for $CaCl_2$. The positive shift observed at low concentrations for $MgCl_2$ and $CaCl_2$ indicate that Mg^+ and Ca^{2+} promote the hydrogen bonded structure of water and at higher concentrations the conditions are not quite favourable for stabilization of water structure. In the entire concentration range studied, ΔT_{obs} for $SrCl_2$ and $BaCl_2$ are negative and increase with increase in the concentration. At any given

concentration ΔT_{obs} for $MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$ indicating that the structure promoting nature of $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$.

The discussion on the results of the studies carriedout on the effect of ammonium halides (NH_4Cl, NH_4Br and NH_4I) on TSVM of water and ΔT_{str} are presented in Section 4.4. ΔT_{obs} is positive for NH_4Cl up to 3.4×10^{-2} and negative thereafter. ΔT_{obs} is negative for NH_4Br and NH_4I in the entire concentration range studied. ΔT_{str} for NH_4Cl varies nonlinearly with concentration. ΔT_{str} for NH_4Br is almost zero up to $w \simeq 3 \times 10^{-2}$ and thereafter become negative. ΔT_{str} for NH_4I is negative throughout the concentration range. At any given concentration ΔT_{str} for $NH_4Cl > NH_4Br > NH_4I$ indicating the structure breaking nature of $I^- > Br^- > Cl^-$.

Literature survey indicates that only the effect of single electrolytes on the temperature of sound velocity maximum of water have been studied extensively. 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 the TSVM of water. The details of the method of evaluation of the ideal shift due to the addition of mixed electrolytes to water are presented in Section 5.1. The results of ultrasonic velocity versus temperature at different concentrations of mixed electrolytes namely (NaCl + KCl), (NaBr + KBr), (NaI + KI), (KCl + KBr), (KBr + KI), (KCl + KI), (NaCl + NaBr), (NaBr + NaI) and (NaCl + NaI) are presented in Section 5.2.

The discussions of the results on the effect of mixed electrolytes (NaCl + KCl), (NaBr + KBr), (NaI + KI), (KCl + KBr), (KBr + KI), (KCl + KI) and (NaCl + NaBr), (NaBr + NaI), (NaCl + NaI) on TSVM of water are presented in Sections 5.3, 5.4 and 5.5 respectively. For all these mixed electrolytes ΔT_{str} have been evaluated. For all the mixed electrolytes, ΔT_{str} have been found to be negative throughout the concentration range studied. At any given concentration, ΔT_{str} are found to be in the order (NaI + KI) > (NaBr + KBr) > (NaCl + KCl) indicating an enhancement in the structure breaking nature of K^+ and a decrement in the structure promoting nature of Na^+ in the presence of halide ions.

It is also observed that at any given concnetration ΔT_{str} for (KBr + KI) > (KCl + KI) > (KCl + KBr) which indicates that in the presence of K^+ the structure breaking nature of halide ions is increased and the increase is in the order $I^- > Br^- > Cl^-$. It is also observed that ΔT_{str} for (NaCl + NaBr) is almost zero within the limits of experimental error at low concentrations and is slightly negative at higher concentrations. ΔT_{str} for (NaBr + NaI) and (NaCl + NaI) are negative throughout the concentration range increasing with increase in the concentration. At any given concentration ΔT_{str} for (NaBr + NaI) > (NaCl + NaI) > (NaCl + NaBr) indicating that the structure promoting nature of Na^+ is balanced and subdued by the presence of halide ions in the order $(Br^- + I^-)$ > $(Cl^- + I^-)$ > $(Cl^- + Br^-)$ consistent with the behaviour of halide ions in disrupting the hydrogen bonded structure of water which is in the ordr $I^- > Br^- > Cl^-$.

To delineate further the effect of unlike ions on each other and on the like ions in aqueous mixed electrolytes, the author has examined the additivity rule by evaluating Δ using the relation

$$\Delta \quad = \quad [\Delta T_{str}]_{ME} - [(\Delta T_{str})_{E1} + (\Delta T_{str})_{E2}]$$

where suffixes E_1, E_2 and ME stand for electrolyte 1, electrolyte 2 and mixed electrolyte respectively. The variations of Δ with concentrations of the mixed electrolytes studied are discussed and interpreted in terms of interaction of like ions on unlike ions in Section 5.3, 5.4 and 5.5.

The studies carriedout illustrate the usefulness of temperature of sound velocity maximum data in aqueous solutions electrolytes and mixed electrolytes in understanding the solution structure and delineating ion-ion and ion-solvent interactions and classification of ions as structure makers and structure breakers.

Ultrasonic velocity measurements have been carriedout by various workers throughout the composition range in completely miscible systems of water and nonelectrolytes. However, the measurements have been quite extensive in the water rich region because of the peculiarities exhibited in this region. In the organic rich region, the number of measurements are fewer and do not extend to infinite dilution of water. Most of the data simply show a linear variation in the mole fraction range 0.9 to 1.0 of the organic solute in water. It will be interesting to see how the solution structure would be at infinite dilution of water in nonelectrolytes as revealed from ultrasonic measurements. It is from this angle the author studied the ultrasonic

velocity behaviour of dilute solutions of water in a few nonelectrolytes namely PEG (poly ethylene glycol) - 200, PEG - 300, PEG - 400, PEG - 600, diethylene glycol, methanol, ethanol, n-butanol, 2-methoxy ethanol, 2-ethoxy ethanol, 2-butoxy ethanol, diethyl amine, triethyl amine, dibutyl amine and di-sec-butyl amine at 298.15 K and forms Part II of the thesis. A brief review of the work carriedout on the ultrasonic behaviour of binary mixtures of water and nonelectrolytes is presented in Chapter 6.

Chapter 7 deals with the experimental methods used in the present study. The method of measurement of ultrasonic velocity at 298.15 K in dilute solutions of water in nonelectrolytes is detailed in Section 7.1. The measured velocities have been corrected for diffraction effects. The organic liquids used in the present study are purified following standard procedures and the purity of the samples have been tested by measuring their density at 298.15 K using bicapillary type pycnometer. These details are presented in Section 7.2. The diffraction corrected ultrasonic velocity data of pure liquids at 298.15 K obtained in the present study are compared with literature data in Section 7.3.

The formula which is thermodynamically consistent is employed in evaluating excess sound velocities in dilute solutions of water in nonelectrolytes. The theoretical aspects regarding evaluation of excess sound velocity are presented in Section 8.1. The ultrasonic velocity and excess ultrasonic velocity as a function of mole fraction of water in dilute solutions of water in nonelectrolytes are given in Section 8.2.

Chapter 9 deals with the discussion of the results on the concentration dependence of ultrasonic velocity (u) and excess ultrasonic velocity (u^E) in dilute solutions of water in nonelectrolytes. The discussions on the ultrasonic behaviour of dilute solutions of water in glycols, n-alcohols, 2-alkoxy ethanols and amines are presented in Section 9.1 to 9.4 respectively. In all these systems both the ultrasonic velocity and excess ultrasonic velocity vary nonlinearly with concentration signifying water-water and water-nonelectrolyte associations. At infinite dilution the concentration dependence of u and u^E are linear indicating the existence of water molecules as monomers. Beyond certain optimum concentrations u and u^E vary nonlinearly either almost remaining constant or varying very slowly up to certain extent beyond which both u and u^E vary linearly with concentration of water. The ultrasonic behaviour of the solutions in the region between these optimum concentrations has been interpreted as due to formation water - nonelectrolyte complexes or existence of islands of water clusters of varying size distributed uniformly throughout the solution. The variation of u and u^E at higher concentration range of water has been attributed to the existence of water as polymeric molecules distributed uniformly throughout the solution.

The present study indicates that useful information regarding the structure of dilute solutions of water in nonelectrolytes can be obtained from ultrasonic velocity data.