SUMMARY

The thesis entitled " Transport and thermodynamic properties of sugar solutions in aqueous NH_4Cl at different temperatures ", consists measurements of the densities, viscosities and ultrasonic velocities of glucose, fructose, maltose and sucrose solutions in water and in 0.5M aqueous ammonium chloride at different temperatures. The study has been undertaken with a view to investigate solute-solute, solute-solvent and solvent-solvent interactions in these solutions. The effect of concentration as well temperature of measurement on these interactions have been also reported.

First chapter of the thesis is devoted to the historical development of solution chemistry. An account has been also taken of different theories of viscosity, molar volumes and ultrasonic velocity of solutions.

In chapter second detailed descriptions of experimental techniques used to measure the viscosity, density and ultrasonic velocity through these solutions are given. Viscosity density and ultrasonic velocity of these solutions are measured in thermostated water

bath having thermal stability of $\pm$ 0.01 ^{o}C, using Ostwald's viscometer, bicapillary pycnometer and M-82 ultrasonic interferrometer having frequency 1.5 MH_z with an accuracy of $\pm$ 0.0003 Cp, $\pm$ 0.0001 gm/ml and 0.03% respectively. The efflux times are measured with a stop watch corrected to 0.01 second. The viscometer, pycnometer and ultrasonic velocity cell are caliberated with the help of triplly distilled water.

In chapter third viscosities, densities and ultrasonic velocities of 0.5M aqueous ammonium chloride solutions are reported at various temperatures. The relative viscosities of 0.5M aqueous ammonium chloride solutions at various temperatures are compared with those reported previously. Our values of relative viscosities, η_r, agreed well with those reported previously. From ultrasonic velocities and densities of 0.5M aqueous ammonium chloride solutions at various temperatures, different thermodynamic parameters such as adiabatic compressibilities (β_{ad}), apparent molar compressibility (ϕ_K), inter free length (L_f), specific acoustic impedance (Z), solvation number (Sn) and apparent molar volume (ϕ_V) have been calculated using various equations. These parameters show that ammonium chloride acts as structure breaker in water.

Molar volumes of glucose, fructose, maltose and sucrose in water and in 0.5M aqueous ammonium chloride solutions are calculated by using density data with the help of equation of the following form

$$\phi_V = \frac{1000(\rho_0 - \rho)}{C \times \rho_0} + \frac{M_2}{\rho_0}$$

The apparent molar volumes (ϕ_V) of all sugar solutions in both solvents at all temperatures are found to vary linearly with concentration (C) of the sugar. The limiting apparent molar volume at infinite dilution (ϕ_V^0) which is equal to partial molar volume of solute at infinite dilution ($\overline{V}_2^0$) are obtained as a intercept of linear plots of ϕ_V versus C. All these ϕ_V^0 values are positive suggesting the structure promoting tendencies of all sugars in both solvents. This is further confirmed from the sign of $d^2\phi_V^0/dT^2$ which is popularly known as Hepler criterion for structure breaking/making nature of added solute. These ϕ_V^0 values are fitted in polynomial equation of temperature. The limiting apparent molar expansibility (ϕ_E^0) are calculated from $d^2\phi_V^0/dT^2$ values.

The variation of ϕ_E^0 with temperature for all systems is found to be linear suggesting that all sugars exhibit caging effect in both solvents. The volumes of transfer ($\phi_{V(tr.)}^0$) of these carbohydrates for water to 0.5M aqueous solutions have been calculated with the help of equation

$$\phi_V^0 \text{ (transfer)} = \phi_V^0 \text{ (0.5M aqueous } NH_4Cl) - \phi_V^0 \text{ (aqueous)}$$

These ϕ_V^0 values are interpreted with the use of cosphere overlap model of Friedman and Krishnann. The ϕ_V^0 values are also explained with the help of equation of Shahidi et al

$$\phi_V^0 = V_{VW} + V_V - V_S$$

where V_{VW} is Van der waal's volume, V_V is volume associated with void and V_S is volume due to shrinkage.

In chapter fifth viscosity data of all these sugar solutions at all temperatures are reported. Viscosity data of glucose and fructose, solutions in both solvents and at all temperatures are analysed with the help of Jones-Dole equations of the form

i) $\eta_r = 1 + AC^{\frac{1}{2}} + BC$

and

ii) $\eta_r = 1 + BC$

for linear plots of $\eta_r - 1/\sqrt{C}$ versus $\sqrt{C}$, Coefficients 'A' and 'B' are obtained as intercepts and slopes of these plots. It has been observed that $A/B \ll 1$, and hence same viscosity data is further analysed with the help the equation

$$\eta_r = 1 + B\,C,$$

The viscosity coefficients 'B' are obtained as intercepts of linear plots of η_r versus concentration (C). The viscosity data of these sugar solutions are also fitted into Moulik equation

$$\eta_r^2 = M + K\,C^2$$

and Vand's equation

$$\ln \eta_r = \frac{2.5\,\phi}{1 - K'\phi}$$

The 'B' coefficients obtained from these various equations are positive suggesting the structure promoting tendencies of glucose and fructose in water and in 0.5M aqueous ammonium chloride. Viscosity data of maltose and sucrose solutions in both solvents at all temperatures fit well into modified Jones-Dole and Moulik equations. The 'B' coefficients of these sugars are found to be positive in all cases suggesting that maltose and sucrose behave as structure makers in these solvents. The viscosity data of all these sugar solutions are further analysed with the help of Feakins equation

$$B = \frac{\bar{V}_1^{0} - \bar{V}_2^{0}}{1000} + \frac{\bar{V}_1^{0}}{1000}\left(\frac{\Delta\mu_1^{0*} - \Delta\mu_2^{0*}}{RT}\right)$$

From the values of $\Delta\mu_2^{0*}$ all these sugars are found to be structure promoter in both solvents at all temperatures.

In chapter sixth the ultrasonic velocity measurements of sugar solutions in water and in 0.5M aqueous ammonium chloride solution at 25, 30, 35 and 40 ^{o}C are reported. The ultrasonic velocity (U) and density (ρ) of these solutions are used to calculate different thermodynamic parameters such as βad , ϕ_K

L_f, Z, R_A and Sn. The variation of ultrasonic velocity with concentration ($\frac{dU}{dC}$) is explained with the help of equation

$$\frac{dU}{dC} = -\frac{U}{2}\left[\frac{1}{\rho}\frac{d\rho}{dC} + \frac{1}{\beta_{ad}}\left(\frac{d\beta_{ad}}{dC}\right)\right]$$

The change of ultrasonic velocity with change in free length in all these sugar solutions are explained with the help of Eyring and Kincaid model. **Adiabatic** compressibility of these solutions are found to obey Bachem's relation

$$\beta_{ad} = \overset{0}{\beta}_{ad} + AC + BC^{3/2}$$

constants 'A' and 'B' of Bachem's relations are obtained as intercepts and slopes of linear plots of $\beta_{ad} - \overset{0}{\beta}_{ad}/_C$ versus $\sqrt{C}$. Apparent molar compressibilities, ϕ_K , are analysed with the help of Gücker's law

$$\phi_K = \overset{0}{\phi}_K + S_K C$$

The $\overset{0}{\phi}_K$ values are obtained as intercepts of linear plots of ϕ_K versus concentration (C). All these $\overset{0}{\phi}_K$ values are found to be negative indicating strong interaction between solute and solvent molecules through dipole-dipole interactions. The relative association R_A in all the cases is found to increase with increase in concentration and temperature, suggesting the predomination of solvation of solute molecules over breaking of solvent aggregates. The variation of specific acoustic impedance (Z) with concentration and temperature is explained in the light of Eucken's theory. Hydration number (Sn) of all sugars in both solvents are positive indicating appriciable solvation of sugars. The hydration number of all sugars in salt solutions are higher than those in water because of simultaneous hydration of ammonium chloride ions as well as sugar molecules. The change in hydration number with temperature is due to loss of coordinated water molecules at higher temperatures.