

CHAPTER 3

3.1 Properties of 0.5M Aqueous Ammonium Chloride as Solvent:

Measurements of viscosities, apparent molar volumes and ultrasonic velocities in solutions provide excellent tools of obtaining data of solute-solute and solute-solvent interactions. These interactions have been studied in aqueous and nonaqueous solutions by many workers employing several physico-chemical methods¹⁻³. Such investigations in mixed solvents are also reported by many investigators in recent times, but these studies in solutions of electrolyte solutions as solvents are scanty. Since multicomponent solutions are widely used in industries and in biofluides, the study of their physical properties is a matter of interest, both for practical and theoretical point of views. The situation becomes more interesting, if non-electrolyte is present in aqueous solutions of electrolyte. Pioneering work in such ternary system has been done by Robinson and Stokes^{4,5}. Similar studies have also been undertaken by various workers, employing conductance, density, viscosity and ultrasonic

velocity measurements.

The present work has been carried out on multi-component system containing ammonium chloride-sugar-water, to investigate the dependence of thermodynamic and transport properties of sugar solutions in aqueous electrolyte solution, on concentration and temperature of solutions.

The attenuation coefficient (α) of longitudinal ultrasonic wave propagating along (100) in single crystal ammonium chloride has been measured⁶ as a function of frequency from 5 to 55 Mc/sec and as a function of temperature from 200 to 270 °k. Cynoweth and Schneider⁷ studied the adiabatic elastic constant of single crystal ammonium chloride as a function of sound frequency from 5 to 55 Mc/sec and as a function of temperature from 150 to 300 °k. Ammonium chloride goes through a lambda transition at $T \sim 243$ °k. The partial molar volumes and viscosities of aqueous ammonium chloride solutions are reported by Stokes⁸, Goldsack and Franchetto⁹. Electrical conductivity and viscosity of ethyl and methyl alcohol solutions of ammonium chloride and ammonium iodide have been reported by Denprov¹⁰. The specific gravity and viscosity of water-methyl alcohol (or ethyl alcohol)-ammonium chloride (or ammonium iodide) have

been experimentally measured at 15 to 25 °C. It has been found that ammonium chloride increases the viscosity of alcoholic solution and ammonium iodide decreases it. The electrical conductance of solution decreased with the proportion of alcohol in solution. The rate of decrease was found much greater in concentrated solution. The concentration and temperature dependence of viscosities of aqueous solutions of strong electrolytes such as KI, NH₄Cl and Na₂SO₄ have been investigated by Kaminsky¹¹. The Ubbelohd viscometer was used to determine relative viscosities (η_r) of solutions of KI, NH₄Cl, Na₂SO₄ in concentration range .001 to 0.5 mole/liter and in the temperature range 15 - 40 °C. The increase of η_r with rising temperature has been explained qualitatively with the help of structure breaking and hydration effects. The viscosities of aqueous electrolyte solutions of chloride, bromide, iodide salts of lithium, sodium, potassium, ammonium, rubidium and cesium cations at 298.15 °K have been analyzed with the help of Jones-Dole equation¹². The viscosity B coefficient was obtained graphically and related to sum of partial molal entropies of ions present. The variation of the relative viscosity, η_r , of concentrated aqueous solution of 1:1 electrolyte with electrolyte

concentration is represented by general equation with the help of extended limiting equation of Einstein¹³. Empirical equation relating B and \bar{V} of electrolyte in aqueous solution is obtained by least square analysis. This empirical equation resembles more closely to the equation of the form $B \sim 2.5 \bar{V}$. Assuming applicability of this equation to ions in solutions, the hydration numbers of ions have been calculated and their dependence of ionic radii, ionic molar volumes and ionic B_{\pm} have been discussed in the light of structure-making and structure-breaking properties of ions in solutions.

3.2 Methods and Materials:

The ammonium chloride was recrystallized from triple distilled water and was dried in air for 24 hour at room temperature. 0.5M aqueous ammonium chloride solution was prepared by dissolving accurately weighed amount of ammonium chloride in triple distilled water. This solution was allowed to stand for some time in order to attain thermal equilibrium. The density, viscosity and ultrasonic velocity of 0.5M aqueous ammonium chloride solution were measured with the help of bicapillary pycnometer,

Ostwald viscometer and Mittal's M-81 ultrasonic interferometer respectively. Accuracy in measurements was $\pm 5 \times 10^{-5}$ gm/ml, $\pm .003$ Cp and $\pm 0.03\%$ respectively. The measurements were carried out at 25, 30, 35 and 40 °C with the thermal stability of ± 0.01 °C. For viscosity measurements, efflux times were measured with the help of stop watch accurate to $\pm .01$ second. An efflux times were more than 100 s, hence kinetic energy correction was not necessary.

3.3 Results and Discussion:

Table 3.1 includes relative viscosities (η_r) and ultrasonic velocities (U) of 0.5M aqueous ammonium chloride solution at 25, 30, 35 and 40 °C. From observation of table 3.1, it is seen that the relative viscosity value (0.9946) at 25 °C is slightly deviating from that reported by Sahu and Behera¹⁴ (0.9964).

Relative viscosities of 0.5M aqueous ammonium chloride solution increases with temperature suggesting the decreased solute-solvent interaction at high temperature.

The ultrasonic velocities in these solutions are found

to increase with increase of temperature. This can be attributed to weakening in already strong solute-solvent interactions with rise in temperature.

Different thermodynamic parameters such as adiabatic compressibility (β_{ad}), apparent molar compressibility (Φ_k), intermolecular free length (L_f), specific acoustic impedance (Z), solvation number (S_n) and apparent molar volume (Φ_v) have been calculated at 25, 30, 35 and 40 °C, using ultrasonic velocity (U) and density (ρ) of these solutions with the help of following equations^{15,16}

$$\beta_{ad} = \frac{1}{u^2 \times \rho} \quad \text{--- (3.1)}$$

$$L_f = k \sqrt{\beta_{ad}} \quad \text{--- (3.2)}$$

$$\Phi_k = \frac{1000}{c \times \rho_0} \left(\rho_0 \beta_{ad} - \beta_{ad}^0 \rho \right) \frac{\beta_{ad}^0 \times M_2}{\rho_0} \quad \text{--- (3.3)}$$

$$R = \frac{\bar{M}}{\rho} \times u^{1/3} \quad \text{--- (3.4)}$$

where $\bar{M} = \sum_i M_i x_i$

$$Z = u \times \rho \quad \text{--- (3.5)}$$

$$R_A = \frac{\rho}{\rho_0} \left(\frac{u_0}{u} \right)^{1/3} \quad \text{--- (3.6)}$$

Table-3.1 Relative viscosities (η_r) and ultrasonic velocities of 0.5M aqueous ammonium chloride solution at different temperatures.

Parameter	Temperature °C			
	25	30	35	40
η_r	0.9946	1.00113	1.0035	1.00689
U, m/sec	1521.18	1530.07	1541.53	1545.65

$$S_m = \frac{n_1}{n_2} \left(1 - \frac{\beta_{ad}}{\beta_{ad}^0} \right) \quad \text{--- (3.7)}$$

$$S_m = -\phi_K / \beta_{ad}^0 \times \frac{M_2}{\rho_0} \quad \text{--- (3.8)}$$

$$\phi_v = \frac{1000(\rho_0 - \rho)}{C \times \rho_0} + \frac{M_2}{\rho_0} \quad \text{--- (3.9)}$$

Where ρ , ρ_0 and u , u_0 are density and ultrasonic velocities of solution and solvent respectively; M_2 , the molecular weight of solute; β_{ad}^0 and β_{ad} , the adiabatic compressibility of solvent and solution; K is Jacobson's constant, C , concentration in mole/liters, n_1 and n_2 are number of moles of solvent and solute respectively; \bar{M} is the average molecular weight of solution expressed by

$$\bar{M} = M_1 X_1 + M_2 X_2 \quad \text{--- (3.10)}$$

Where M_1 is molecular weight of solvent, X_1 and X_2 are mole fractions of solvent and solute respectively.

The experimental values of ultrasonic parameters and density of 0.5M aqueous ammonium chloride solutions at different temperatures are presented in Table 3.2.

It is seen that value of ' Z ' increases^{17,18}, while β_{ad} decreases, if u increases with temperature. The

Table-3.2 Density, Ultrasonic velocity and related parameters of 0.5M aqueous ammonium chloride at different temperatures.

Parameters	Temperature °C			
	25	30	35	40
ρ g/cc	1.00535	1.00391	1.00227	1.00045
U m/sec	1521.18	1530.07	1541.53	1545.65
$Z \times 10^{-5}$ CGS units	1.5298	1.5326	1.5450	1.5463
R cm/sec	972.62	975.93	979.98	982.68
$L_F A^\circ$	0.4097	0.4116	0.4121	0.4146
$\beta_{ad} \times 10^{12}$ cm ² /dyne	42.9854	42.5483	41.9866	41.8390
R_A	1.00188	1.00266	1.00413	1.00415
S_n	1.01878	0.8384	0.53802	0.37878
$\phi_K \times 10^9$ cm ² /dyne	-2.460	-1.998	-1.210	-0.88
ϕ_V c c	36.99	37.11	37.22	37.32

behaviour observed in present study is perhaps due to much weaker solute-solvent interaction at high temperature. The increase in free length with increase of temperature supports the above conclusion. The apparent molar compressibility values are found to be negative at all temperatures. This suggests aggregation of solvent molecules around solute supporting strong solute-solvent interactions. The apparent molar compressibility values increase with increase of temperature indicating that electrostrictive solute-solvent interaction decreases with increase of temperature. Solvation numbers (S_n) are positive at all temperatures suggesting appreciable hydration of ions, here added electrolyte behaves as structure promoter. The weakening of solute-solvent interaction with rise in temperature is further confirmed from decrease of solvation number with increase of temperature. The molar sound velocity (R) increases with temperature, confirming the decrease of solute-solvent interactions at elevated temperatures. The relative association (R_A) is influenced by two factors (1) the breaking up of the solvent molecules on addition of electrolyte to it and (2) the solvation of ions that are simultaneously present. The former resulting in a decrease and later in increase of

relative association. In the present investigation, relative association increases with temperature. As temperature of solution rises, the aggregates of water molecules breakdown resulting in increased hydration of ions by free water molecules and hence increase in R_A with increase in temperatures.

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