

Chapter – III

Experimental Section

3.1. Chemicals Used: Their Sources and Purification

3.1.1. Solvents

Water was first deionized and then distilled from an all glass distilling set using alkaline KMnO_4 solution. The double distilled water was then finally distilled using an all glass distilling set. Precautions were taken to prevent contamination from CO_2 and other impurities. The triply distilled (TD) water had specific conductance less than $1 \times 10^{-6} \text{ ohm}^{-1}\text{cm}^{-1}$.

1,4 dioxane, Merck, India, was kept several days over potassium hydroxide(KOH). This was followed by refluxing over excess of sodium for 12 hours. Finally, the dioxane was distilled from sodium. The pure compound had a boiling point of 374.5 /760 mm, a density of $1.0292 \text{ g. cm}^{-3}$ at 298.15 K, a co- efficient of viscosity of 1.196 cp. at 298.15 K.

Tetrahydrofuran (THF), Merck, India was kept several days over potassium hydroxide (KOH), refluxed for 24 hours and distilled over LiAlH_4 as described earlier.¹ The purified solvent has boiling point of 339 K/760 mm, a density of $0.88072 \text{ g cm}^{-3}$, a coefficient of viscosity $0.46300 \times 10^2 \text{ m Pa. S}$ and a specific conductance of Ca. $0.81 \times 10^{-6} \text{ S cm}$ at 298K.

Methanol (E. Merck, India, Urasol grade) was dried over 3\AA molecular sieves and distilled fractionally. Middle fraction was collected and redistilled. The purified solvent had a density of $0.78654 \text{ g. cm}^{-3}$ and a coefficient with viscosity of 0.545 m. Pa. s at 298.15 K, these values are in good agreement with the literature values which are $0.7866 \text{ g. cm}^{-3}$ and 0.5445 m. Pa. s. respectively.

Dimethylsulphoxide, Merck, India, was kept several days over anhydrous CaSO_4 refluxed for 4 hours over CaO . Finally, it was distilled at low pressure. The pure compound had a boiling point of 463 K/760 mm, a density of 1.1 g. cm^{-3} at 298.15 K, a co-efficient of viscosity of 1.96 cp. at 298.15 K.

3.1.2. Mixed Solvents

The mixed solvents containing 10, 20, 30, 40, 60, 80, 100 mass % of THF + H₂O mixtures were prepared accurately by mixing the requisite amounts of THF and H₂O by weight. The physical properties of THF and its different mass% at different temperatures are recorded in Table 1.

Besides these solvent mixtures, other various solvent mixtures such as DMSO + H₂O, 1, 4 dioxane + H₂O, THF + monoalcohols, CH₃OH + H₂O, tetrahydrofuran + benzene + methanol, iso-propanol + n-Hexane + benzene etc. have been used for my present research studies, their purifications and physical properties have been discussed in the respective chapters.

3.1.3. Electrolytes

Tetraalkylammonium salts were of Fluka's purum or puriss grade and purified in the manner given in the literature.^{2,3} Generally the salts were purified by recrystallisation. The bromide salts of higher tertaalkyl homologues were recrystallised second time to ensure highest purity. The crystallised salts were dried in vacuum. The salts were stored in glass bottles in darkened dessicator over fused CaCl₂.

Tetraethylammonium bromide (Et₄NBr) (Fluka, Purum) was crystallised from methanol and dried at 363 K for 24 hours.

Tetrapropylammonium bromide (Pr₄NBr) (Fluka, purum) was dissolved in a minimum volume of methanol, reprecipitated from dry ether and dried at 363 K for 48 hours.

Lithium and sodium bromides and chlorides, ammonium chlorides and bromides (Sd's fine chemicals) were of purum or puriss grade and were purified as described earlier.⁴

Some mineral salts viz., ammonium nitrate, Lithium nitrate, sodium nitrate potassium nitrate, magnesium nitrate and Calcium nitrates A.R. Sd. Fine chemicals were used as such, only after drying over P₂O₅ in a desicator for more than 48 hours.

3.2. Experimental Techniques

3.2.1. Ultrasonic Velocity Measurements

Sound velocities were measured, with an accuracy of 0.3%, using a single-crystal variable-path ultrasonic interferometer (Mittal Enterprise, New

Delhi) operating at 4 MHz, which was calibrated with water, methanol and benzene at each temperature. The temperature stability was maintained within $\pm 0.01^\circ\text{C}$ by circulating thermostated water around the cell by a circulating pump. The thermostatic bath was maintained with an accuracy of $\pm 0.01^\circ\text{C}$ of the desired temperature, as described earlier.

The principle used in the measurement of the sound velocity (u) is based on the accurate determination of the wavelength (λ) in the medium. Ultrasonic waves of known frequency (γ) are produced by a quartz crystal fixed at the bottom of the cell. These waves are reflected by a movable metallic plate kept parallel to the quartz crystal.

If the separation between these two plates is exactly a whole multiple of the sound wavelength, standing waves are formed in the medium. This acoustic resonance gives rise to an electrical reaction on the generator driving the quartz crystal and the anode current of the generator becomes maximum. If the distance is now increased or decreased and the variation is exactly one half wave length ($\lambda/2$) or integral multiple of it, anode current again becomes maximum. From the knowledge of the wave length (λ), the velocity (u) can be obtained by the relation.

$$\text{Velocity (u)} = \text{Wave Length } (\lambda) \times \text{Frequency } (\gamma) \quad (1)$$

Isentropic Compressibility (K_s) can then be calculated by the following formula:

$$K_s = 1/(u^2\rho) \quad (2)$$

Where ρ is the density of the experimental liquid.

The ultrasonic interferometer consists of the following two parts, (i) the high frequency generator, and (ii) the measuring cell. The measuring cell is connected to the output terminal of the high frequency generator through a shielded cable. The cell is filled with the experimental liquid before switching on the generator. The ultrasonic waves move normal or the quartz crystal till they are reflected back from the movable plate and the standing waves are formed in the liquid in between the reflector plate and the quartz crystal.

The micrometer is slowly moved till the anode current on the high frequency generator shows a maximum. A number of maximum readings of anode current are passed on and their number (n) is counted. The total distance (r) thus moved by the micrometer gives the value of wavelength (λ) with the following relation.

$$r = n \times \lambda/2$$

3.2.2. Density Measurements

Densities were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25cm³ and an internal diameter of the capillary of about 1 mm. The pycnometer was calibrated at 25, 30, 34, 40, 45 and 50°C with doubly distilled water. The precision of the density measurements was $\pm 3 \times 10^{-5}$ g.cm³.

The measurements were carried out in a thermostatic water bath maintained with an accuracy of $\pm 0.01^\circ\text{C}$ of the desired temperature.⁵ A 60 w heating element and a toluene-mercury thermo-regulator were used to maintain the temperature of the experimental thermostat which was placed in a hot-cum-cold thermostat. The temperature of the hot-cum-cold thermostat was preset at the desired temperature using a contact thermometer and relay system. The absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge.⁶

3.2.3. Measurements of Viscosity

The kinematic viscosities were measured by means of a suspended-level Ubbelohde⁷ viscometer with a flow time of about 539s for distilled water at 25°C. The time of efflux was measured with a stop watch capable of recording O.I.S. The viscometer was always kept in a vertical position in a water thermostat. The viscometer needed no correction for kinetic energy. The kinematic viscosity (γ) and the absolute viscosity (η) are given by the following equations.

$$\gamma = ct - k/t \quad (3)$$

$$\eta = \gamma\rho \quad (4)$$

where, t is the efflux time, ρ is the density and c and k are the characteristic constants of the viscometer. The values of the constants c and k , determined by using water and methanol as the calibration liquids at 25°C and 30°C were found to be 2.08605×10^{-3} and 5.69261 respectively. The precision of the viscosity was $\pm 0.05\%$. In all cases, the experiments were performed in at least five replicates and the results were averaged.

Relative viscosities (η_r) were obtained using the equation

$$\eta_r = \eta/\eta_0 = \rho t/\rho_0 t_0 \quad (5)$$

where η , η_0 , ρ , ρ_0 and t , t_0 are the absolute viscosities, densities and flow times for the solution and solvent respectively.

The measurements were carried out in a thermostatic water bath maintained with an accuracy of $\pm 0.01^\circ\text{C}$ of the desired temperature.

3.2.4. Conductance Measurements

Conductance measurements were carried out on Philips Pye-Unicam PW 9509 conductivity water at a frequency of 2000 Hz using a dip-type cell of cell constant 1.14cm^{-1} and having an accuracy of 0.01%. The instrument was standardized using standard KCl solutions. The cell was calibrated by the method of Lind and co-workers.⁸ The conductivity cell was sealed to the side of a 500cm^3 conical flask closed by a ground glass fitted with a side arm through which dry and pure nitrogen gas was passed to prevent admission of air into the cell when solvent or solution was added. The measurements were made in an oil bath maintained at the required temperature $\pm 0.005^\circ\text{C}$ by means of a mercury in glass thermoregulator.

Solutions were prepared mass for the conductance runs, the molalities being converted to molarities by the use of densities measured as described above. Several independent solutions were prepared and runs were performed to ensure the reproducibility of the results. Due correction was made for the specific conductance of the solvent at all temperatures.

References

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