

CHAPTER III

EXPERIMENTAL SECTION

CHEMICALS USED : THEIR SOURCES AND PURIFICATION

3.1.1 Electrolytes

The salts were of Fluka's purum or puriss grade. Lithium chloride (LiCl), lithium bromide (LiBr), lithium iodide (LiI), lithium tetrafluoroborate (LiBF₄) and lithium hexafluoroarsenate (LiAsF₆) were dried under vacuum at high temperature for 48 hours and were used without further purification. Lithium perchlorate (LiClO₄) was recrystallized three times from conductivity water and then dried under vacuum for several days.¹

Tetraalkylammonium salts were purified in the manner given in the literature.^{2,3} Generally these salts were purified by recrystallization. Higher tetraalkyl homologues were recrystallized second time to ensure the highest purity. The crystallized salts were dried in vacuum and stored in glass bottles in darkened dessicator over fused CaCl₂.

Tetraethylammonium bromide (Et₄NBr) was recrystallized from methanol and dried at 363K for 24 hours.

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

Tetrabutylammonium bromide (Bu₄NBr) was taken in a minimum volume of acetone. Ether was added to the solution till the commencement of precipitation. The

solution was then cooled and the resulting crystals were filtered. After a preliminary drying, the salt was finally grounded in a mortar and dried at 333K for 48 hours.

Tetrapentylammonium bromide (Pen_4NBr) was recrystallized from acetone + ether mixtures and dried in vacuo at 333K for 48 hours.

Tetrahexylammonium bromide (Hex_4NBr) and tetraheptylammonium bromide (Hep_4NBr) were washed with ether and dried in vacuo at room temperature for 48 hours.

Tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) was prepared by precipitation from tetrabutylammonium bromide (Bu_4NBr) and sodium tetraphenylborate (NaBPh_4) in water and the precipitate was washed five times by water. The bulky white precipitate was dried in vacuo at 353K for 48 hours.⁴

Sodium tetraphenylborate (NaBPh_4) was recrystallized three times from acetone and dried in vacuo at 353K for 72 hours.

Potassium tetraphenylborate (KBPh_4) was prepared by mixing equimolar aqueous solutions of potassium nitrate (KNO_3) and sodium tetraphenylborate (NaBPh_4). The product was recrystallized from 30 mass percentage aqueous acetone and dried in vacuo for several weeks.

The alkali-metal bromides – sodium bromide (NaBr), potassium bromide (KBr), rubidium bromide (RbBr) and cesium bromide (CsBr) were dried in vacuo for a long time immediately prior to use and were used without further purification.

3.1.2 Solvents

N,N-Dimethylacetamide (DMA, E.Merck, India, >99.5%) was shaken well with charged CaO (A.R.BDH) for 1-2 hours, decanted, and distilled twice⁵ and the middle fraction was collected and used. Its density ($0.93644 \text{ g cm}^{-3}$) and viscosity (0.9330 mPa-s) at 298.15K , compared well with the literature values which are 0.9366 g cm^{-3} and 0.919 mPa-s respectively.⁶ The relative permittivity of N,N-dimethylacetamide ($\epsilon = 37.78$) at 298.15K was taken from the literature.⁶

Formamide (E. Merck. Germany, > 99%) was dried over freshly ignited quicklime for several hours and then distilled over reduced pressure and the purified solvent had a density 1.1254 g.cm^{-3} and viscosity 2.9527 mPa-s at 298.15K .⁶

N,N-Dimethylformamide (E Merck. India) was kept overnight with phosphorous pentoxide, decanted and distilled over nitrogen. The purified solvent had a density of $0.94362 \text{ g cm}^{-3}$ and viscosity 0.80240 mPa-s at 298.15K . All these values are in good agreement with the literature values.⁶

2-Ethoxyethanol (E.Merck, India) was kept overnight with anhydrous K_2CO_3 , decanted and distilled in an all glass distillation set and the middle fraction was collected. The purified solvent had a density $0.9252 \text{ g. cm}^{-3}$ and a viscosity 1.8243 mPa-s at 298.15K .⁷

3.2 EXPERIMENTAL TECHNIQUES

3.2.1 Density Measurements

Densities were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm³ and an internal diameter of the capillary of about 1 mm. The pycnometer was calibrated at 25, 35 and 45°C with doubly distilled water. Measurements were made using a single pan Mettler balance with an accuracy of ± 0.00001 g. 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.⁸ The reproducibility of density measurements was $\pm 3 \times 10^{-5}$ gm cm⁻³.

3.2.2 Viscosity Measurements

The kinematic viscosities were measured by means of a suspended-level Ubbelohde⁹ 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 0.1s. The viscometer was always kept in a vertical position in a water thermostat. The viscometer needed no correction for kinetic energy. The kinematic viscosity (ν) and the absolute viscosity (η) are given by the following equations :

$$\nu = ct - k/t \quad (1)$$

$$\eta = \nu \rho \quad (2)$$

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 benzene as the calibration liquids at 25, 35 and 45°C were found to be $1.648 \times 10^{-5} \text{ cm}^2\text{s}^2$ and -0.02331647 cm^2 respectively. The precision of the viscosity measurements was 0.05%. In all cases experiments were performed in at least five replicates and the results were averaged.

Relative viscosities (η_r) were obtained using the equation :

$$\eta_r = \eta / \eta_o = \rho t / \rho_o t_o \quad (3)$$

where, η , η_o , ρ , ρ_o and t , t_o 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 within an accuracy of $\pm 0.01^\circ\text{C}$ of the desired temperature.

3.2.3 Conductance Measurements

Conductance measurements were carried out with a Philips Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip-type cell of cell constant 1.14 cm^{-1} and having an accuracy of 0.1%. The instrument was calibrated using standard KCl solutions. The cell was calibrated by the method of Lind and co-workers.¹⁰ the conductivity cell was sealed to the side of a 500 cm^3 conical flask closed by a ground glass fitted with a side arm through which dry and pure nitrogen was passed to prevent admission of air into the cell when solvent of solution was added. The measurements were made in an oil bath maintained at the required temperatures $\pm 0.005^\circ\text{C}$ by means of a mercury in glass thermoregulator.^{11,12}

Solutions were prepared by 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.

3.2.4 Ultrasonic Velocity Measurements

Sound velocities were measured,^{13,14} with an accuracy of $\pm 0.3\%$ using a single-crystal variable-path ultrasonic interferometer (Mittal Enterprises, New Delhi) operating at 4 MHz, which was calibrated with water, methanol, and benzene at each temperature. The temperature stability was maintained at $\pm 0.01^\circ\text{C}$ by circulating thermostated water around the cell by a circulating pump.

The principle used in the measurement of the sound velocity (u) is based on the accurate determination of the wave length (λ) in the medium. Ultrasonic waves of known frequency (ν) 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 wave length, 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 wavelength ($\lambda/2$) 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 :

$$\text{Velocity (u)} = \text{Wave length } (\lambda) \times \text{Frequency (v)} \quad (4)$$

Isentropic compressibility (k_s) can then be calculated by the following formula :

$$k_s = 1 / (u^2 \rho) \quad (5)$$

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 from 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 :

$$r = n \times \lambda / 2 \quad (6)$$

3.2.5 Spectroscopic Measurements

The FTIR spectra in the region $4000\text{-}500\text{ cm}^{-1}$ were recorded on a Bomem da-8.02 FTIR Spectrophotometer using potassium bromide window in a capillary cell construction. For each sample, fifty scans were accumulated and the results averaged. The spectra were recorded by the Regional Sophisticated Instrumentation centre, North Eastern Hill University, Shillong. All spectra were scanned at least twice to ensure repeatability. The wave number resolution in spectral acquisition was 1 cm^{-1} . The FT Raman spectra were recorded by the Regional sophisticated Instrumentation centre, Indian Institute of Technology, Madras. The samples were excited at 1064 nm using a Nd : YAG laser and Brucker IFS 66V optical bench with an FRA 106 Raman module attached to it. Laser power was set at 200 mw , and 250 (averaged) scans were accumulated with a resolution of 2 cm^{-1} .

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