

## **CHAPTER III**

### **Experimental Section**

#### **3.1. Chemicals Used: Their Sources And Purification**

##### **Solvents**

Tetrahydrofuran [Merck, India] was kept for several days over KOH, refluxed for 24 hours and distilled over  $\text{LiAlH}_4$  <sup>(1)</sup>. The boiling point ( $66^\circ\text{C}$ ), density ( $0.8807 \text{ g.cm}^3$ ) and viscosity ( $0.46300 \text{ mP.s}$ ) compared well with the literature values <sup>(2)</sup>. The specific conductance of THF was  $\sim 0.81 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$  at  $25^\circ\text{C}$ .

1, 2-Dimethoxyethane (Fluka, Purrum) was shaken with  $\text{FeSO}_4$  (AR, BDH) for 1-2 h, decanted and distilled. The distillate was refluxed for 12 h and redistilled over metallic sodium <sup>(3)</sup> and the middle fraction was collected. The purity of the solvent as checked by gas chromatography was found to be  $>99.8\%$ . Its boiling point ( $84.5^\circ\text{C}$ ), density ( $0.86109 \text{ g.cm}^{-3}$ ) and viscosity ( $0.4089 \text{ mPa.s}$ ) compared well with literature values <sup>(3-4)</sup>.

2-Methoxyethanol was allowed to stand overnight with  $\text{CaSO}_4$  and distilled from Sodium. Before fractional distillation the solvent was treated with 2, 4-dinitrophenylhydrazine <sup>(5)</sup>. The purity of liquid was checked by gas chromatography and purified liquid had a density of  $0.95772 \text{ g.cm}^{-3}$  at  $30^\circ\text{C}$ , viscosity  $1.39329 \text{ mPa.s}$  at  $30^\circ\text{C}$  and boiling point  $124.4^\circ\text{C}$  which is compared well with literature values <sup>(5-6)</sup>.

Water was first deionized and then distilled from an all glass distilling set using alkaline  $\text{KMnO}_4$  solution <sup>(7)</sup>. The double distilled water was then finally distilled using an all glass distilling set. Precautions were taken to

prevent contamination from CO<sub>2</sub> and other impurities. The triply distilled (TD) water had specific conductance less than  $1 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ .

Ethane-1, 2-diol (A.R. S.D. Fine) was first dried over fused CaO overnight and then distilled twice under vacuum. The middle fraction was further dried using 4A<sup>0</sup> molecular sieves (Linde) and stored and protected against moisture and CO<sub>2</sub> <sup>(8)</sup>. The pure compound had a boiling point of 197.4°C, a density of 1.1098 g cm<sup>3</sup> at 298.15 K, a coefficient of viscosity 16.9 mPa.s at 25<sup>0</sup>C. These values are in excellent agreement with literature values <sup>(2)</sup>.

Aldrich gold label grade glycerol, quoted as 99.5 + % pure, was further distilled under reduced pressure, the temperature at the top of the fractionating column being 140<sup>0</sup>C and the pressure, measured near the receiving flask, being about 0.034 k Pa. The central fraction was used and found to have an electrical conductivity of  $7.4 \times 10^{-9} \text{ S cm}^{-1}$  at 23.9<sup>0</sup>C, this value not being significantly altered by further distillation <sup>(9)</sup>.

Formamide was treated with some bromothymol blue and then neutralized it with NaOH before heating to 80<sup>0</sup>C under reduced pressure to distill off ammonia and water. The amide was again neutralized and the process was repeated until the liquid remained neutral on heating. Sodiumformate was added and the formamide was reduced under reduced pressure at 80<sup>0</sup>C. The distillate was again neutralized and redistilled. It was then fractionally crystd in the absence of CO<sub>2</sub> and water by partial freezing <sup>(5)</sup>. The purified formamide had a boiling point of 210.5<sup>0</sup>C, a density of 1.1292 g.cm<sup>3</sup> at 25<sup>0</sup>C, a coefficient of viscosity 3.302 mPa.s at 25<sup>0</sup>C. These values are in excellent agreement with literature values <sup>(2)</sup>

The solvents, benzene, carbontetrachloride and chloroform were provided by Fluka (>0.99 mole fraction) and these were subjected to no further purification other than drying with Union Carbide 0.4 nm molecular sieves to eliminate residual traces of water and degassing by an ultrasound technique.

Gas chromatography analysis detected no significant peaks of impurities for all the components. The densities and viscosities of pure liquids are compared well with the literature values <sup>(10-13)</sup>.

Monoalcohols (E. Merck, India, uvasol grade, 99.5% pure) were dried over 3A° molecular sieves and distilled fractionally. The middle fraction were collected and redistilled. The purities of the solvents were checked by gas chromatography and the water content were found to be 0.023-0.022-weight %. The density and viscosity of the purified solvent had compared well with the literature values <sup>(13-24)</sup>.

### **Electrolytes**

Alkali metal halides viz. LiBr, NaBr, KBr, KCl, and KI were of Purum or Puriss grade [Fluka] and were used as such after drying over CaO for 48 hours and were used without further purification <sup>(25-26)</sup>.

Resorcinol (A.R.) was also used after drying in desiccators at least 24 hours. The compound was dried and stored in a vacuum condition and was purified by the reported procedure <sup>(27)</sup>.

Tetraalkylammonium bromides were of Purum or Puris grade [Fluka] (Me<sub>4</sub>NBr, Et<sub>4</sub>NBr, Pr<sub>4</sub>NBr, and Bu<sub>4</sub>NBr) were purified by recrystallization and the higher homologs were recrystallized twice to ensure maximum purity. The recrystallized salts were dried *in vacuo* at elevated temperatures for 12 h. Tetrabutylammonium tetraphenylborate was prepared by mixing equimolar quantities of sodium tetraphenylborate (Fluka, Purum) and tetrabutylammonium bromide in aqueous medium. The salts were dried *in vacuo* at 80°C for 48 h. Sodium tetraphenylborate was recrystallized from acetone and dried *in vacuo* at 80°C for 72 h. <sup>(28-29)</sup>.

Lithium nitrate (LiNO<sub>3</sub>), sodium nitrate (NaNO<sub>3</sub>), potassium nitrate KNO<sub>3</sub>, magnesium nitrate Mg (NO<sub>3</sub>)<sub>2</sub>, and calcium nitrate [Ca(NO<sub>3</sub>)<sub>2</sub>] all A.R

grade were used as such, only after drying over  $P_2O_5$  in a desiccator for more than 48 h<sup>(30)</sup>.

## 3.2. Experimental Techniques

### 3.2.1. Density Measurements

Densities ( $\rho$ ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm<sup>3</sup> and an internal diameter of the capillary of about 1mm. The pycnometer was calibrated at 298.15, 303.15, 308.15, 313.15, 318.15, and 323.15 K with triply distilled water and benzene. The precision of the density measurements was  $\pm 3 \times 10^{-5}$  g cm<sup>-3</sup>. The pycnometer with the test solution was equilibrated in thermostatic water bath maintained at  $\pm 0.01^\circ\text{C}$  of the desired temperature by means of mercury in glass thermo regulator and the temperature was determined with a calibrated thermometer and a Muller bridge<sup>(31)</sup>.

### 3.2.2. Viscosity Measurements

The kinematic viscosities were measured at  $25 \pm 0.01^\circ\text{C}$ ,  $30 \pm 0.01^\circ\text{C}$ ,  $35 \pm 0.01^\circ\text{C}$ ,  $40 \pm 0.01^\circ\text{C}$ ,  $45 \pm 0.01^\circ\text{C}$  and  $50 \pm 0.01^\circ\text{C}$  using a suspended Ubbelohde type viscometer<sup>(32)</sup> with a precision of  $\pm 0.05\%$  and it was calibrated at the desired temperatures with water and methanol. The time of efflux was measured with a stopwatch 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 kinematics viscosity ( $\nu$ ) and the absolute viscosity ( $\eta$ ) are given by the following equations:

$$\nu = Kt - L/t \quad (1)$$

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

where,  $t$  is the efflux time,  $\rho$  is the density and  $K$  and  $L$  are the characteristic constants of the viscometer. The values of the constants  $K$  and  $L$ , determined by using water and benzene as the calibration liquids at 25, 35, and 45°C, were found to be  $2.12935 \times 10^{-3} \text{ cm}^2 \cdot \text{s}^2$  and  $4.67424 \text{ cm}^2$  respectively. The precision of the viscosity measurements was  $\pm 0.05\%$ . In all cases, the experiments were performed in at least five replicates and the results were averaged.

To calculate the relative viscosities ( $\eta_r$ ) the following equation was used.

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

where,  $\eta$ ,  $\eta_o$ ,  $\rho$ ,  $\rho_o$  and  $t$ ,  $t_o$  be 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 accuracy  $\pm 0.01^\circ\text{C}$  of the desired temperature as described earlier.

### 3.2.3. Conductance Measurements

Conductance measurements were carried out on a Systemic-308 conductivity meter at a frequency of 4 mHz using a dip-type cell (cell constant  $0.1 \text{ cm}^{-1}$ ) with an accuracy of  $\pm 0.1\%$ . The cell was calibrated by the method of Lind and co-workers<sup>(33)</sup> using aqueous potassium chloride solutions. Measurements were made in an oil bath maintained at the required temperatures  $\pm 0.01^\circ\text{C}$  as described in the literature<sup>(13, 34)</sup>. Several independent solutions were prepared, and conductance measurements were performed with each of these to ensure the reproducibility of the results. Corrections were made for the specific conductances for the solvent.

In order to minimize moisture contamination, all solutions were prepared in a dehumidified room with utmost care.

### 3.2.4. Ultrasonic Sound Speeds Measurements

The speeds of sound ( $u$ ) in pure liquids and solutions were measured with multi-frequency ultrasonic interferometer (supplied by Mittal Enterprise, New Delhi) with an accuracy of  $\pm 0.3\%$ . In the present work, a steel cell fitted with a quartz crystal of 2 MHz<sup>(35)</sup> - frequency was employed. This was calibrated with water, methanol, and benzene at the desired temperatures. The temperature stability was maintained within  $\pm 0.01^\circ\text{C}$  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 wavelength ( $\lambda$ ) in the medium. Ultrasonic waves of known frequency ( $\gamma$ ) are produced by a quartz crystal fixed at the bottom of the cell. A movable metallic plate kept parallel to the quartz crystal reflects these waves. 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 wavelengths ( $\lambda/2$ ) or integral multiple of it, anode current again becomes maximum. From the knowledge of the wavelength ( $\lambda$ ), the velocity ( $u$ ) can be obtained by the relation:

$$\text{Velocity } (u) = \text{Wavelength } (\lambda) \times \text{Frequency } (\gamma) \quad (4)$$

Isentropic compressibility ( $K_S$ ) can then be calculated by the following relation:

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

where  $\rho$  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 an 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 ( $\rho$ ) thus moved by the micrometer gives the value of wavelength ( $\lambda$ ) with the following relation:

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

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