# CHAPTER III

## EXPERIMENTAL SECTION

### 3.1 CHEMICALS USED : THEIR SOURCES AND PURIFICATION

### 3.1.1 Electrolytes

Lithium tetrafluoroborate ($LiBF_4$, G.R. E. Merck) and sodium tetrafluoroborate ($NaBF_4$, Fluka, purum) were dried under vacuum at high temperatures for 48 hours and were used without further purification.

Potassium picrate (KPic) was prepared[1] by neutralizing picric acid (A.R., BDH) with an equal amount of potassium hydroxide (A.R., BDH) in ethanol. The resulting potassium picrate, which precipitated, was recrystallized from water and dried *in vacuo* for 3 – 4 weeks.

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

Sodium perchlorate ($NaClO_4$, Fluka, purum) was recrystallized several times from water and methanol mixtures and dried *in vacuo* at 423 K for 96 hours.

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

Tetraphenylarsonium picrate (Ph$_4$AsPic) was prepared by the metathesis between potassium picrate obtained as above and tetraphenylarsonium chloride (Ph$_4$AsCl, Fluka, pro analysis), both dissolved in 50 mass percentage aqueous ethanol. The precipitate was washed with water, repeatedly recrystallized from ethanol, and dried *in vacuo* for several weeks.

Tetrabutylammonium tetraphenylborate (Bu$_4$NBPh$_4$) was prepared by precipitation from tetrabutylammonium bromide (Bu$_4$NBr, Fluka, puriss) and sodium tetraphenylborate (NaBPh$_4$, Fluka, puriss) in water and the precipitate was washed five times by water. The bulky white precipitate was dried *in vacuo* at 353 K for 48 hours.[2]

Tetraphenylarsonium chloride (Ph$_4$AsCl, Fluka, pro analysis) was recrystallized from absolute ethanol solution by dry ether twice and dried *in vacuo*.[3]

Tetraphenylphosphonium chloride (Ph$_4$PCl, Fluka, purum), and tetraphenylphosphonium bromide (Ph$_4$PBr, Fluka, purum) were dissolved in absolute ethanol, reprecipitated by the addition of dry ether, and vacuum dried at 333 K for 48 hours (melting point 570-571 K).[2]

### 3.1.2 Solvents

2-Methoxyethanol (ME) (G.R. E.Merck) was dried with potassium carbonate and distilled twice in an all glass distillation set immediately before use and the middle fraction collected. The purified solvent had a density of 0.96002 g cm$^{-3}$ and a coefficient

of viscosity of 1.5414 mPa s at 298.15 K. These values are in good agreement with the literature values,[4] which are 0.96028 g cm$^{-3}$ and 1.543 mPa s respectively.

1,2-Dimethoxyethane (DME, Fluka, purum) was shaken well with FeSO$_4$ (A.R., BDH) for 1-2 hours, decanted and distilled. The distillate was refluxed for 12 hours and redistilled over metallic sodium.[5] The boiling point (357.65 K) and density (0.86132 g cm$^{-3}$ at 298.15 K) compared fairly well with the corresponding literature values,[6] which are 358.15 K and 0.86120 g cm$^{-3}$ respectively.

N-Methylacetamide (NMA, G.R. E. Merck, Germany) was purified by fractional distillation over nitrogen. Its density (0.94224 g cm$^{-3}$ at 313.15 K) and viscosity (3.0038 mPa s at 313.15 K) compared well with the literature values[7] which are 0.9420 g cm$^{-3}$ and 3.02 mPa s at 313.15 K, respectively.

N,N- Dimethylacetamide (DMA, E. Merck, India) was shaken well with charged CaO (A.R. BDH) for 1-2 hours, decanted, and distilled twice. The middle fraction was collected and used. Its density (0.93669 g cm$^{-3}$) and viscosity (0.9271 mPa s) at 298.15 K, compared well with the literature values which are 0.9366 g cm$^{-3}$ and 0.919 mPa s, respectively.[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 cm$^3$ 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. The precision of the density measurements was $\pm 3 \times 10^{-5}$ g cm$^{-3}$.

The measurements were carried out in a thermostatic water bath maintained with an accuracy of $\pm 0.01°$ C of the desired temperature.[8] 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.[9]

## 3.2.2 Viscosity Measurements

The kinematic viscosities were measured by means of a suspended-level Ubbelohde[10] viscometer with a flow time of about 539 s for distilled water at 25° C. The time of efflux was measured with a stop watch capable of recording 0.1 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 ($\nu$) and the absolute viscosity ($\eta$) are given by the following equations:

$$\nu = ct - k/t \tag{1}$$

$$\eta = \nu \rho \tag{2}$$

where, t is the efflux time, $\rho$ 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 $1.648 \times 10^{-5}$ cm$^2$ s$^2$ and $-0.02331647$ 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.

Relative viscosities ($\eta_r$) were obtained using the equation:

$$\eta_r = \eta/\eta_0 = \rho_t / \rho_0 t_0 \tag{3}$$

where, $\eta$, $\eta_0$, $\rho$, $\rho_0$ 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° C of the desired temperature, as described earlier.

### 3.2.3 Conductance Measurements

Conductance measurements were carried out on 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 standardized using standard KCl solutions. The cell was calibrated by the method of Lind and co-workers.[11] 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 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 temperatures ± 0.005°C by means of a mercury in glass thermoregulator.

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, with an accuracy of 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 within ± 0.01 ° C by circulating thermostated water around the cell by a circulating pump. The thermostatic bath was maintained with an accuracy of ± 0.01°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 ($\lambda$) in the medium. Ultrasonic waves of known frequency ($\gamma$) 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 wavelength ($\lambda/2$) 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:

$$\text{Velocity (u)} = \text{Wavelength } (\lambda) \text{ x Frequency } (\gamma) \tag{4}$$

Isentropic compressibility ($\kappa_s$) can then be calculated by the following formula:

$$\kappa_s = 1/(u^2\rho) \tag{5}$$

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 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 ($\lambda$) with the following relation:

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

### 3.2.5 Spectroscopic Measurements

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 66 V optical bench with an FRA 106 Raman module attached to it. Laser power was set at 200mW, and 250 (averaged) scans were accumulated with a resolution of 2 cm$^{-1}$.

## References

1. S. Tirumala and J. T. Davis, *J. Am. Chem. Soc.*, **119**, 2769, 1997.

2. M. Castagnolo, A. Sacco and A. D. Giglio, *J. Chem. Soc., Faraday Trans. I*, **80**, 2669, 1984.

3. G. Kalfoglou and L. H. Bowen, *J. Phys. Chem.*, **73**, 2728, 1969.

4. L. Tassi, *J. Chem. Soc., Faraday Trans.*, **89**, 733, 1993.

5. S. K. Ghosh, D. K. Hazra and S. C. Lahiri, *Thermochim.Acta*, **147** , 41,1989.

6. E. Renard and J. C. Justice, *J. Soln. Chem.*, **3**, 633, 1974.

7. *Physical Chemistry of Organic Solvent Systems*, Eds. A. K. Covington and T. Dickinson, Plenum Press, New York, 1973, p.4.

8. S. K. Ghosh and D. K. Hazra, *Ind. J. Chem.*, **29 A**, 656, 1990.

9. D. Dasgupta, S. Das and D. K. Hazra, *J. Chem. Soc., Faraday Trans.1*, **84**, 1057, 1988.

10. J. R. Suindells, J. R. Coe Jr. and T. B.Godfrey, *J. Res. Natd. Bur.Stand.*, **48**, 1, 1952.

11. J. E. Lind Jr, J. J. Zwolenik and R. M. Fuoss, *J. Chem. Soc.*, **81**, 1557, 1959.