

## CHAPTER III

### **Experimental Section**

#### **3.1. Source and Purification of the Chemicals used**

##### **3.1.1. Solvents**

Water was first deionized and then distilled from an all glass distilling set using alkaline  $\text{KMnO}_4$  solution. The double distilled water was then finally distilled using an all glass distilling set. Precautions were taken to prevent contamination from  $\text{CO}_2$  and other impurities. The triply distilled water had specific conductance less than  $1 \times 10^{-6} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$ .

1,3-Dioxolane ( $\text{C}_3\text{H}_6\text{O}_2$ ), M.W. 74.08, LR, India, was heated under reflux with  $\text{PbO}_2$  for 2 hrs., then cooled and filtered. After adding xylene to the filtrate, the mixture was fractionally distilled<sup>1,2</sup>. The solvent obtained after purification had a boiling point of 348 K / 760 mm, a density of 1058.6  $\text{g. cm}^{-3}$  and a coefficient of viscosity of 0.00575 P at 298.15 K.

1,4-Dioxane (DO,  $\text{C}_4\text{H}_8\text{O}_2$ ), M.W. 88.11, Merck, India, was kept several days over potassium hydroxide (KOH). This was followed by refluxing over excess of sodium for 12 hours. Finally, it was distilled from sodium. The pure compound had a boiling point of 375 K / 760 mm, a density of 1027.3  $\text{kg. m}^{-3}$  and a coefficient of viscosity of 0.01196 P at 298.15 K.

Tetrahydrofuran (THF,  $\text{C}_4\text{H}_8\text{O}$ ), M.W. 72.11, Merck, India was kept several days over potassium hydroxide (KOH), refluxed for 24 hours and distilled over  $\text{LiAlH}_4$ . The purified solvent had boiling point of 339 K / 760 mm, a density of 880.7  $\text{kg. m}^{-3}$  and a coefficient of viscosity 0.00463 P at 298.15 K.

Ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ), M.W. 62.07, LR, India, was first dried over fused  $\text{CaO}$  overnight. It was further dried using 4Å molecular sieves (Linde) and then distilled under vacuum. The solvent had boiling point of 471 K / 760 mm and 341 K / 4 mm, a density of 1106.3  $\text{kg. m}^{-3}$  and a coefficient of viscosity 0.16388 P at 298.15 K.

N,N-Dimethylformamide (DMF,  $\text{C}_3\text{H}_7\text{NO}$ ), M.W. 73.10, Merck, India, was refluxed at high temperature for 24 hrs. with triphenylchlorosilane, then it was distilled at low pressure. The solvent had boiling point of 426 K / 760

mm and 349 K / 39 mm, a density of 946.1 kg. m<sup>-3</sup> and a coefficient of viscosity 0.00859 P at 298.15 K.

Dimethylsulphoxide (DMSO, C<sub>2</sub>H<sub>6</sub>SO), M.W. 78.13, Merck, India, was kept several days over anhydrous CaSO<sub>4</sub>, 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 and 349 K / 12 mm, a density of 1095.4 kg. m<sup>-3</sup> and a co-efficient of viscosity of 0.02042 P at 298.15 K.

n-Hexane (C<sub>6</sub>H<sub>14</sub>), M.W. 86.20, LR, India, was washed with fuming H<sub>2</sub>SO<sub>4</sub>, dried and distilled from sodium hydride. The pure compound had a boiling point of 342 K / 760 mm, a density of 660.0 kg. m<sup>-3</sup> and a co-efficient of viscosity of 0.02814 P at 298.15 K.

Benzene (C<sub>6</sub>H<sub>6</sub>), M.W. 78.10, LR, India, was at first washed with conc. H<sub>2</sub>SO<sub>4</sub> and then with aqueous NaOH. After drying with P<sub>2</sub>O<sub>5</sub> it was distilled. The solvent had a boiling point of 353 K / 760 mm, a density of 8722 kg. m<sup>-3</sup> and a co-efficient of viscosity of 0.05881 P at 298.15 K.

The Alcohols used for the experimental purposes i.e. methanol (MeOH, CH<sub>3</sub>OH, M.W. 32.04), ethanol (EtOH, C<sub>2</sub>H<sub>5</sub>OH, M.W. 46.07), 1-propanol (1-PrOH, C<sub>3</sub>H<sub>7</sub>OH, M.W. 60.10), 2-propanol (2-PrOH, C<sub>3</sub>H<sub>7</sub>OH, M.W. 60.10), 1-butanol (1-BuOH, C<sub>4</sub>H<sub>9</sub>OH, M.W. 74.12), 2-butanol (2-BuOH, C<sub>4</sub>H<sub>9</sub>OH, M.W. 74.12), t-butanol (t-BuOH, C<sub>4</sub>H<sub>9</sub>OH, M.W. 74.12) and i-amyl alcohol (i-AmOH, C<sub>5</sub>H<sub>11</sub>OH, M.W. 88.15), (Merck, India, Urasol grade) were dried over 4Å molecular sieves and then distilled fractionally. Middle fraction was collected and redistilled.

The purified solvents had densities and viscosities which were in good agreement with the literature values<sup>2,3</sup>. The purity of the solvents finally obtained were > 99.5 %.

The research work has been carried out with single solvents like 1,4-dioxane, i-amyl alcohol along with binary solvent mixtures such as 1,3-dioxolane + alcohols, 1,4-dioxane + H<sub>2</sub>O, tetrahydrofuran + methanol, ethylene glycol + tetrahydrofuran, ethylene glycol + 1,4-dioxane and also with ternary solvent mixtures which includes 1,3-dioxolane + H<sub>2</sub>O + alcohols, tetrahydrofuran + benzene + methanol, iso-propanol + n-hexane + benzene, H<sub>2</sub>O + ethylene glycol + tetrahydrofuran/1, 4-dioxane/N, N-dimethylformamide/dimethylsulphoxide.

The mixed solvents containing various mass % of the pure solvents were prepared accurately by mixing their requisite amounts by weight.

### 3.1.2. Solutes

Tetraalkylammonium salts viz. tetramethylammonium chloride ( $\text{Me}_4\text{NCl}$ , M.W. 109.60), tetraethylammonium bromide ( $\text{Et}_4\text{NBr}$ , M.W. 210.16), tetrapropylammonium bromide ( $\text{Pr}_4\text{NBr}$ , M.W. 266.27), tetrabutylammonium bromide ( $\text{Bu}_4\text{NBr}$ , M.W. 322.37), and tetrabutylammonium iodide ( $\text{Bu}_4\text{NI}$ , M.W. 369.38) were of Fluka's purum or puriss grade and purified in the manner given in the literature<sup>1,4-6</sup>. Generally the salts were purified by recrystallisation. The bromide salts of higher tetraalkyl 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 desiccator over fused  $\text{CaCl}_2$ .

The tetramethylammonium salt was crystallized from ethanol/ethyl ether and dried in a vacuum desiccator. The tetraethylammonium salt was crystallized from ethanol/ethyl ether and dried over  $\text{P}_2\text{O}_5$  in vacuum for several days. The tetrapropylammonium salt was crystallized from ethanol/ethyl acetate and dried at 383 K under reduced pressure. The tetrabutylammonium salts were crystallized from acetone/ethyl ether and dried in vacuum at 363 K for 48 hours.

Lithium bromide ( $\text{LiBr}$ , M.W. 86.85) and ammonium bromide ( $\text{NH}_4\text{Br}$ , M.W. 97.95) (SD fine chemicals) were of purum or puriss grade and were purified as described earlier<sup>6</sup>. These were dried at ~ 80-100°C in vacuum oven for 48 hrs before use.

Sodium iodide salt ( $\text{NaI}$ , Merck, M.W. 149.89) was dissolved in acetone, filtered and cooled to -20°C, the resulting yellow crystals being filtered off and heated in a vacuum oven at 70°C for 6 hr to remove acetone. It was then crystallized from very dil.  $\text{NaOH}$ , dried under vacuum, and stored in a desiccator.

The mineral salts viz., ammonium acetate ( $\text{CH}_3\text{COONH}_4$ , M.W. 77.08), lithium acetate ( $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$ , M.W. 102.02), sodium acetate ( $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ , M.W. 136.08) and potassium acetate ( $\text{CH}_3\text{COOK}$ , M.W. 98.14), of A.R. grade were used after drying over  $\text{P}_2\text{O}_5$  in a desiccator for more than 48 hours.

Resorcinol ( $C_6H_6O_2$ , M.W. 110.10) of A.R. grade was crystallized from benzene/ethyl ether. The compound was dried and stored in a vacuum desiccator.

The purity of the salts was detected by gas-liquid chromatography. The purity of the materials finally obtained were  $> 99.0\%$ .

## 3.2. Experimental Method

### 3.2.1. Measurement of Density

Densities ( $\rho$ ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of  $25\text{ cm}^3$  and an internal diameter of the capillary of about 1 mm. The pycnometer was calibrated at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15 K with doubly distilled water and THF. The precision of the density measurement was  $\pm 0.0003\%$ .

The measurements were carried out in a thermostatic water bath (Science India, Kolkata) maintained with an accuracy of  $\pm 0.01\text{ K}$  of the desired temperature. A 60W heating element and a toluene-mercury thermostat 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<sup>7-9</sup>.

### 3.2.2. Measurement of Viscosity

The kinematic viscosities were measured by means of a suspended-level Ubbelohde<sup>10</sup> viscometer. The time of flow was measured with a stop watch. The viscometer was always kept in a vertical position in the water-bath. The viscometer needed no correction for kinetic energy. The kinematic viscosity ( $\gamma$ ) and the absolute viscosity ( $\eta$ ) are given by the following equations.

$$\gamma = k t - l/t \quad \dots\dots\dots(1)$$

$$\eta = \gamma \cdot \rho \quad \dots\dots\dots(2)$$

where,  $t$  is the time of flow,  $\rho$  is the density and  $k$  and  $l$  are the characteristic constants of the particular viscometer. The values of the constants  $k$  and  $l$ , determined by using water and methanol as the calibration liquids were found to be  $1.821400229 \times 10^{-3}$  and  $-12.66485441$  respectively. The precision of the viscosity measurement was  $\pm 0.004\%$ . In all cases, the experiments were performed in at least three replicates and the results were averaged.

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

$$\eta_r = \eta / \eta_0 = \rho t / \rho_0 t_0 \quad \dots\dots\dots(3)$$

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  $\pm 0.01$  K of the desired temperature.

### 3.2.3. Measurement of Ultrasonic Speed

Ultrasonic speeds were measured, with an accuracy of 0.2 %, using a single-crystal variable-path ultrasonic interferometer<sup>11</sup> (Model M-81, Mittal Enterprise, New Delhi) operating at 4 MHz, which was calibrated with water, methanol and benzene at required temperature. The temperature stability was maintained within  $\pm 0.01$  K by circulating thermostatic water around the cell by a circulating pump.

The principle used in the measurement of the ultrasonic speed ( $u$ ) is based on the accurate determination of the wavelength ( $\lambda$ ) in the medium. Ultrasonic waves of known frequency ( $f$ ) 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 a maximum.

If the distance is now increased or decreased and the variation is exactly one half of wave length ( $\lambda/2$ ) or integral multiples of it, anode current becomes maximum. From the knowledge of the wave length ( $\lambda$ ), the speed ( $u$ ) can be obtained by the relation.

$$\text{Ultrasonic speed } (u) = \text{Wave Length } (\lambda) \times \text{Frequency } (f) \quad \dots\dots\dots(4)$$

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 meter on the high frequency generator shows a maximum. A number of maxima readings of anode current are passed and their number ( $n$ ) are counted. The total distance ( $d$ ) thus moved by the micrometer gives the value of the wavelength ( $\lambda$ ) with the following relation.

$$d = n \times \lambda / 2 \quad \dots\dots\dots(5)$$

Further, the velocity is determined from which the isentropic compressibility ( $K_S$ ) is calculated by the following formula:

$$K_S = 1 / (u^2 \cdot \rho) \quad \dots\dots\dots(6)$$

where  $\rho$  is the density of the experimental liquid.

Fig. 1 shows the Multifrequency Ultrasonic Interferometer i.e.

- (a) Cross-section of the measuring cell, (b) Position of reflector vs. crystal current ( Note : The extra peaks in between minima and maxima occurs due to a number of reasons, but these do not effect the value of  $\lambda/2$  ) and
- (c) Electronic circuit diagram of the instrument.

**3.2.4. Measurement of Conductance**

Systronics Conductivity-TDS meter 308 is a microprocessor based instrument used for measuring specific conductivity of solutions. It can provide both automatic and manual temperature compensation. The instrument shows the conductivity of the solution under test at the existing

temperature or with a temperature compensation. Provision for storing the cell constant and the calibrating solution type, is provided with the help of battery back-up. This data can be further used for measuring the conductivity of an unknown solution, without recalibrating the instrument even after switching it off.

The conductance measurements were carried out on this conductivity bridge using a dip-type immersion conductivity cell of cell constant  $1.11\text{cm}^{-1}$ . The entire conductance data were reported at 1 KHz and was found to be  $\pm 0.3\%$  precise. The instrument was standardized using 0.1(M) KCl solution. The cell was calibrated by the method of Lind and co-workers<sup>12</sup>. The conductivity cell was sealed to the side of a  $500\text{cm}^3$  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 a thermostatic water bath maintained at the required temperature with an accuracy of  $\pm 0.01\text{K}$  by means of a mercury in glass thermoregulator<sup>13</sup>.

Solutions were prepared by weight precise to  $\pm 0.02\%$ . The weights were taken on a Mettler electronic analytical balance (AG 285, Switzerland). The molarities being converted to molalities as required. 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 solvents at desired temperatures.

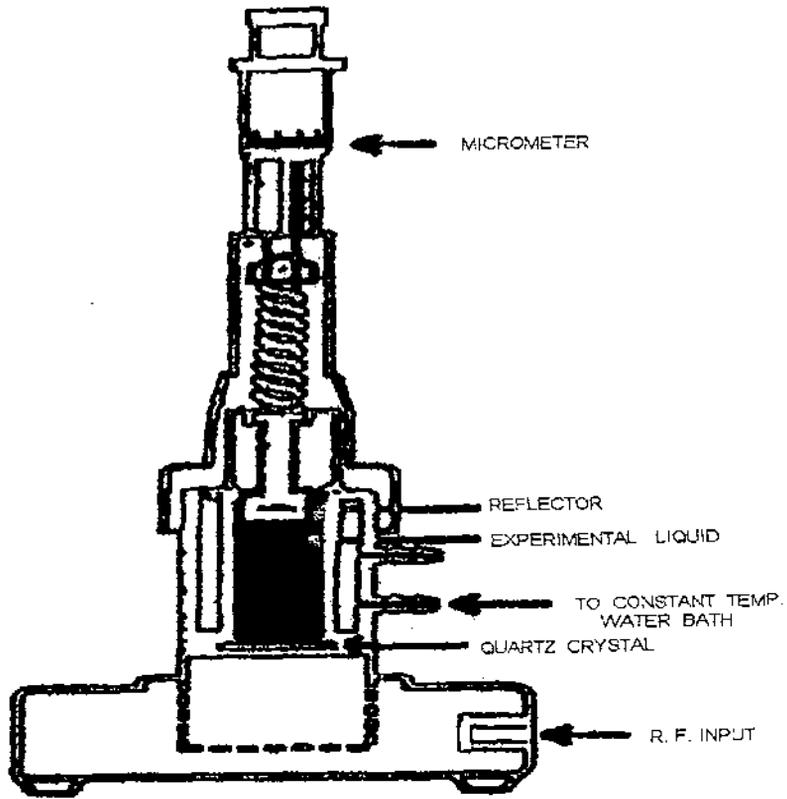
Fig. 2 shows the Systronics Conductivity-TDS meter 308 i.e.

(a) Isometric view and (b) Block diagram of the instrument.

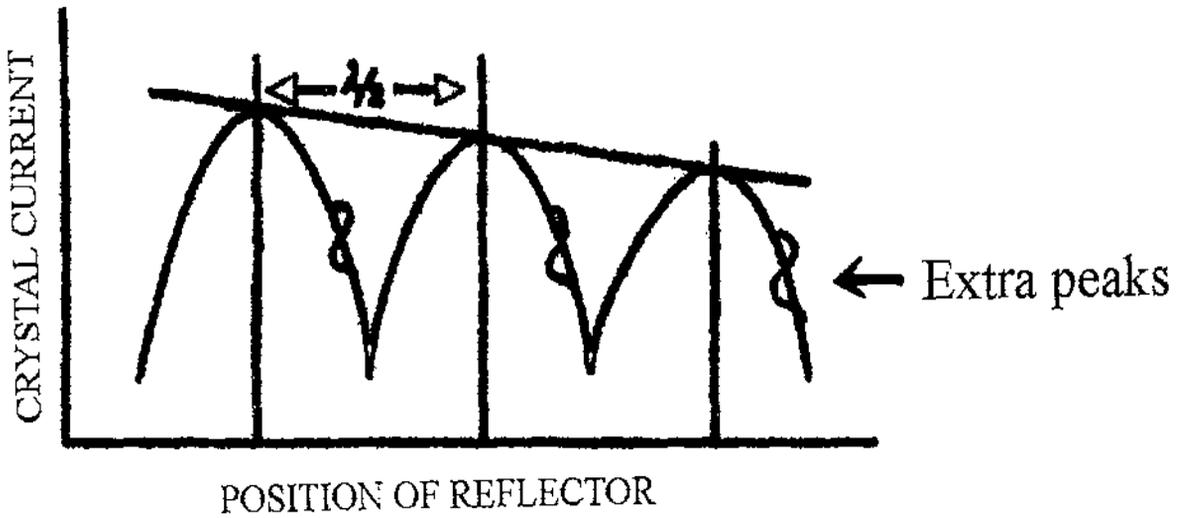
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**Fig.1: The Multifrequency Ultrasonic Interferometer**



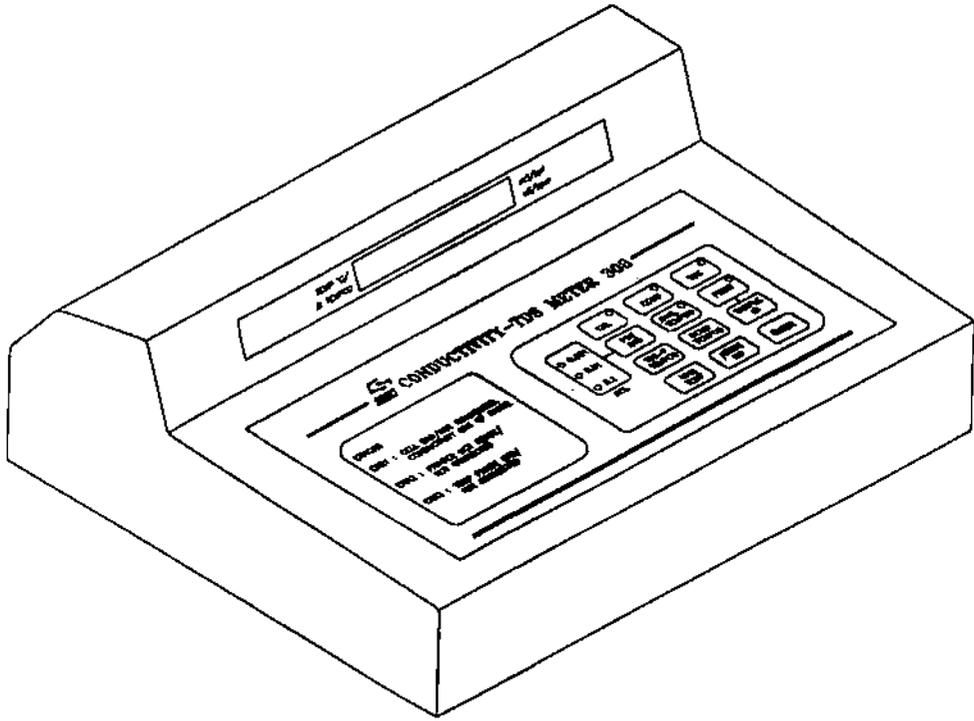
**Fig.1(a): Cross-Section of the Measuring Cell**



**Fig.1(b): Position of Reflector versus Crystal Current**



**Fig.2: The Systronics Conductivity-TDS meter 308**



**Fig.2(a): Isometric View of the Instrument**

Fig.2 (b): Block Diagram of the Instrument

