

CHAPTER III

Experimental Section

3.1. Source and Purification of the Reagents used

3.1.1. *Pure Solvents*

Acetonitrile (ACN, CH_3CN), M.W. 41.05, Merck, India, GR, was distilled from P_2O_5 and then from CaH_2 in an all glass distillation apparatus.¹ The middle fraction was collected. The purified solvent had a density of 776.8 kg. m^{-3} and a coefficient of viscosity 0.3443 mPa.s at 298.15 K which agrees with the literature values.¹

1,4-Dioxane (DO, $\text{C}_4\text{H}_8\text{O}_2$), M.W. 88.11, Merck, India, extrapure, 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.² The pure compound had a density of $1028.7 \text{ kg. m}^{-3}$ and a coefficient of viscosity of 1.1779 mPa.s at 298.15 K , in excellent agreement with literature values.³

1,3-Dioxolane ($\text{C}_3\text{H}_6\text{O}_2$), M.W. 74.08, S.D.Fine chemicals, India, LR, was heated under reflux with PbO_2 for 2 hrs., then cooled and filtered. After adding xylene to the filtrate, the mixture was fractionally distilled⁴. The solvent obtained after purification had a density of $1057.7 \text{ g. cm}^{-3}$ and a coefficient of viscosity of 0.5878 mPa.s at 298.15 K , compared well with literature values⁵.

Tetrahydrofuran (THF, $\text{C}_4\text{H}_8\text{O}$), M.W. 72.11, Merck, India, for synthesis, was kept several days over potassium hydroxide (KOH), refluxed for 24 hours and distilled over LiAlH_4 .⁶ The purified solvent had boiling point of $339 \text{ K} / 760 \text{ mm}$, a density of 880.8 kg. m^{-3} and a coefficient of viscosity 0.4631 mPa.s at 298.15 K .⁷

2-Ethoxyethanol (Cellosolve, $\text{C}_4\text{H}_{10}\text{O}_2$), M.W. 90.12, Merck, India, for synthesis, was kept several days over anhydrous CaSO_4 . Then it was refluxed for 4 h over CaO . Finally, it was distilled at low pressure. Details have been described elsewhere⁸. The pure compound had a density of 925.4 kg. m^{-3} and a coefficient of viscosity of 1.85061 mPa.s at 298.15 K , which agrees with the literature values.^{9,10}

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2-Methoxyethanol (ME, $C_3H_8O_2$), M.W. 79.07, Merck, India, for synthesis, was allowed to stand overnight with $CaSO_4$ and distilled from Sodium. Before fractional distillation the solvent was treated with 2, 4-dinitrophenylhydrazine⁸. The purity of liquid was checked by gas chromatography and purified liquid had a density of 957.7 kg. m^{-3} at 30°C , viscosity 1.39329 mPa.s at 30°C which is compared well with literature values¹¹.

Dimethylsulphoxide¹² (DMSO, C_2H_6SO), M.W. 78.13, 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 density of $1095.1 \text{ kg. m}^{-3}$ and a co-efficient of viscosity of 1.9923 mPa.s at 298.15 K , in well agreement with the literature values.¹³

Monoalcohols (methanol to 1-Octanol), (E. Merck, India, uvasol grade, 99.5% pure) were dried over $3A^\circ$ 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 values¹⁴⁻²⁰.

Normal pentane (C_5H_{12}), M.W. 72.15, hexane(C_6H_{14}), M.W. 86.20, heptane (C_7H_{16}), M.W. 100.20, Merck, India, LR, were purified according to the standard procedures.^{21,22} The purities were checked by density determination dilatometrically. The densities and viscosities of pure liquids are compared well with the literature values^{21,22,23}.

Carbon tetrachloride (CCl_4), M.W. 153.82, Merck, India was shaken vigorously with potassium hydroxide for several hours and was washed with water. This step was repeated for several times and then shaking was done with concentrated sulphuric acid until there was no further coloration, washed again with water, dried with $CaCl_2$, and distilled over P_2O_5 . The density and viscosity values are in excellent agreement with literature values.^{8,22}

tert-butanol, $[(CH_3)_3COH]$, M.W. 74.12, n-butyl acetate, $[CH_3COO(CH_2)_3CH_3]$, M.W. 116.16, 2-butanone, (C_5H_{10}), M.W. 72.15, n-butylamine, $[(CH_3)_3CNH_2]$, M.W. 73.14, (S. D. Fine Chemicals, India, Analytical Reagent, Purity > 99%) were used after drying. The purity of

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the solvents was ascertained by GLC and also by comparing experimental values of densities and viscosities with those reported in the literature²⁴⁻²⁸

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 water had specific conductance less than $1 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$.

3.1.2. *Solutes*

Resorcinol ($\text{C}_6\text{H}_6\text{O}_2$, M.W. 110.10), S.D.Fine chemicals, India, extrapure, was crystallized from benzene/ethyl ether. The compound was dried and stored in a vacuum desiccator²⁹.

The mineral salts viz., ammonium acetate ($\text{CH}_3\text{COONH}_4$, M.W. 77.08), and sodium acetate ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$, M.W. 136.08), Loba Chemie, India, A.R. grade, Lithium acetate ($\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$, M.W. 102.02) and potassium acetate (CH_3COOK , M.W. 98.14), S.D.Fine chemicals, India, LR, were used after drying over P_2O_5 in a desiccator for more than 48 hours.⁸

Lithium chloride (LiCl_3 , M.W.42.39), Merck, India, AR, was recrystallized from conductivity water, dried for several hours at 403 K and stored in a vacuum desiccator.⁸ Sodium chloride (NaCl , M.W. 58.44), BDH, ANALAR, was dried for 48 hours under reduced pressure in presence of P_2O_5 at 473 K without preceding purification and stored under dry nitrogen.⁸ Potassium chloride (KCl , M.W.74.55), Merck, India; LR, crystals were dissolved in conductivity water, filtered, saturated with chlorine and precipitated by HCl after boiling off Excess chlorine. The precipitate was washed, dissolved in conductivity water, recrystallized by cooling to 268 K, dried at room temperature in a vacuum desiccator, fused under dry nitrogen, cooled and stored in a desiccator.⁸

Glycine ($\text{C}_2\text{H}_5\text{NO}_2$, M.W. 75.07), Merck, India; ANALAR, L-alanine ($\text{C}_3\text{H}_7\text{NO}_2$, M.W. 89.06), S.D. Fine Chemicals, India, L-Valine, ($\text{C}_5\text{H}_{11}\text{NO}_2$, M.W. 117.15), Loba Chemie, India, and L-leucine, ($\text{C}_6\text{H}_{13}\text{NO}_2$, M.W. 131.18), Loba Chemie, India, Tetra butyl ammonium bromide [$(\text{C}_4\text{H}_9)_4\text{NBr}$], M.W. 322.37 ,Thomas Baker, India, were used for the present study. These were used without further purification and dried over anhydrous P_2O_5 in a vacuum desiccator before use.

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3.1.3. *mixed Solvents:*

The research work has been carried out with single solvents like 1,4-dioxane, along with binary solvent mixtures such as 2-Ethoxyethanol + monoalcohols (Methanol to 1-Octanol), Acetonitrile + (1,4-dioxane; 1,3-Dioxolane; tetrahydrofuran), H₂O + 1,4-dioxane, H₂O + Carbon tetrachloride, DMSO + (tert-butanol; n-butyl acetate; 2-butanone; n-butylamine), H₂O + Methanol etc.

The mixed solvents were prepared accurately by mixing the requisite volume of 1,4-dioxane and H₂O with earlier conversion of required mass of the respective solvents to volume by using experimental densities of the solvents at experimental temperature. The mixtures were prepared by mixing pure liquids in airtight-stoppered bottles. The density, viscosity and the sound speeds of the mixtures were determined immediately after mixing. The reproducibility in mole fraction was within ± 0.0002 . The physical properties of solvent mixtures at different temperatures are recorded along with literature values (wherever available).

3.2. Experimental Method

3.2.1. *Measurement of Density*

Densities (ρ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm³ and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at 298.15, 303.15, 308.15, 313.15 and 318.15 K with doubly distilled water and benzene using density and viscosity values from the literature.^{30,31} The pycnometer filled with air bubble free experimental liquid was kept vertically in a thermostatic water bath maintained at ± 0.01 K of the desired temperatures for few minutes to attain thermal equilibrium. The pycnometer was then removed from the thermostatic bath, properly dried, and weighed. Adequate precautions were taken to avoid evaporation losses during the time of actual measurements. An average of triplicate measurements was taken into account. Mass measurements accurate to ± 0.01 mg were made on a digital electronic analytical balance (Mettler, AG 285, Switzerland). The precision of the density measurement was $\pm 3 \times 10^{-4}$ g.cm⁻³.

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The temperature of the thermostatic water bath was preset at the desired temperature by using a contact thermometer and relay system. The absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge.³² The solutions were prepared by mixing known volume of pure liquids in airtight-stopper bottles and each solution thus prepared was distributed into three recipients to perform all the measurements in triplicate, with the aim of the determining possible dispersion of the results obtained. Details of methods and techniques of density measurement is given in the literature.^{33, 34-37}

3.2.2. Measurement of Viscosity

The kinematic viscosities were measured by means of a suspended-level Ubbelohde³⁸ viscometer. The time of efflux of a constant volume of the experimental liquid through the capillary was measured with the aid of a Racer stop watch capable of measuring times accurate to ± 0.1 s. The viscometer was always kept in a vertical position in the thermostatic bath with an accuracy of ± 0.01 K of the desired temperature. The efflux time for water at 298.15 K was measured to be 428.9 s. The flow times of pure liquids and liquid mixtures were measured a number of times and the average of the readings was taken into account.

The kinematic viscosity (ν) and the absolute viscosity (η) are given by the following equations.

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

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

where t is the average time of flow, ρ 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 calibrating liquids, were found to be 2.1040×10^{-3} and 11.5477 respectively. The kinetic energy corrections were done from these values and they were found to be negligible.

Relative viscosities (η_r) were obtained using the equation:

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

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 uncertainty in the viscosity measurements,

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based on our work on several pure liquids, was $\pm 2 \times 10^{-4}$ mPa.s. Figure 1 shows a suspended-level Ubbelohde viscometer used in our works.

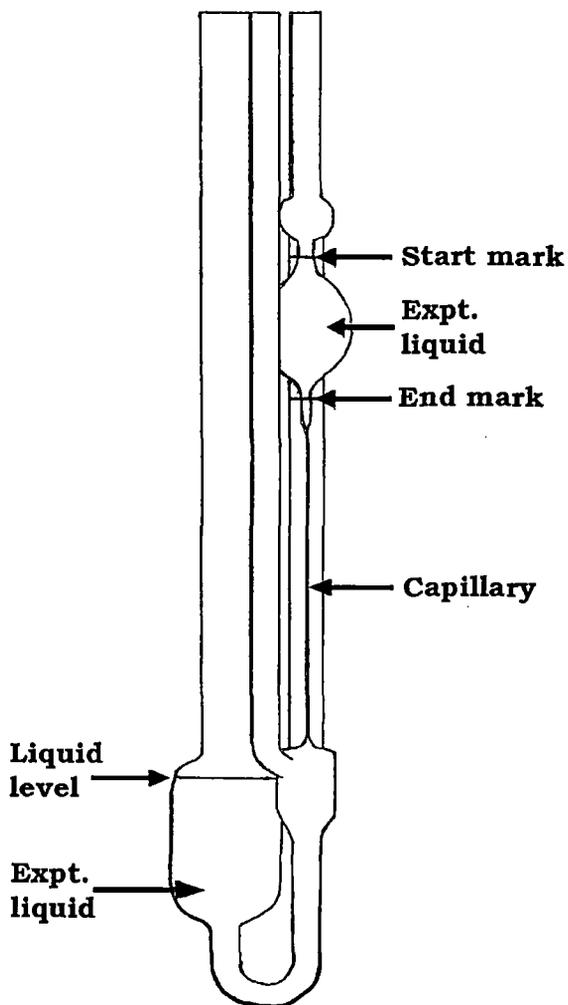


Figure 1. A suspended-level Ubbelohde viscometer.

3.2.3. Measurement of Ultrasonic Speed

Ultrasonic speeds were measured, with an accuracy of 0.2 %, using a single-crystal variable-path ultrasonic interferometer³⁹ (Model M-81, Mittal Enterprise, New Delhi) operating at 4 MHz, which was calibrated with water, methanol and benzene at the

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experimental temperature. The temperature stability was maintained within ± 0.01 K by circulating thermostatic water around the cell with the aid of a circulating pump.

The principle used in the measurement of the ultrasonic speed (u) is based on the accurate determination of the wavelength (λ) 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 originates an electrical reaction on the generator driving the quartz crystal and the anode current of the generator becomes a maximum.

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

$$u = \lambda \times f \quad (4)$$

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 deflects a maximum. A number of maxima of anode current are observed and their number (n) is counted. The total distance (d) thus moved by the micrometer gives the value of the wavelength (λ) with the following relation.

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

Further, the speed (u) determined thus is used for the calculation of the isentropic compressibility (K_s) using the following formula:

$$K_s = 1/(u^2 \rho) \quad (6)$$

where ρ is the density of the experimental liquid.

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Figure 2 shows a Multi-frequency Ultrasonic Interferometer i.e. (A) Cross-section of the measuring cell and (B) Position of reflector vs. crystal current.

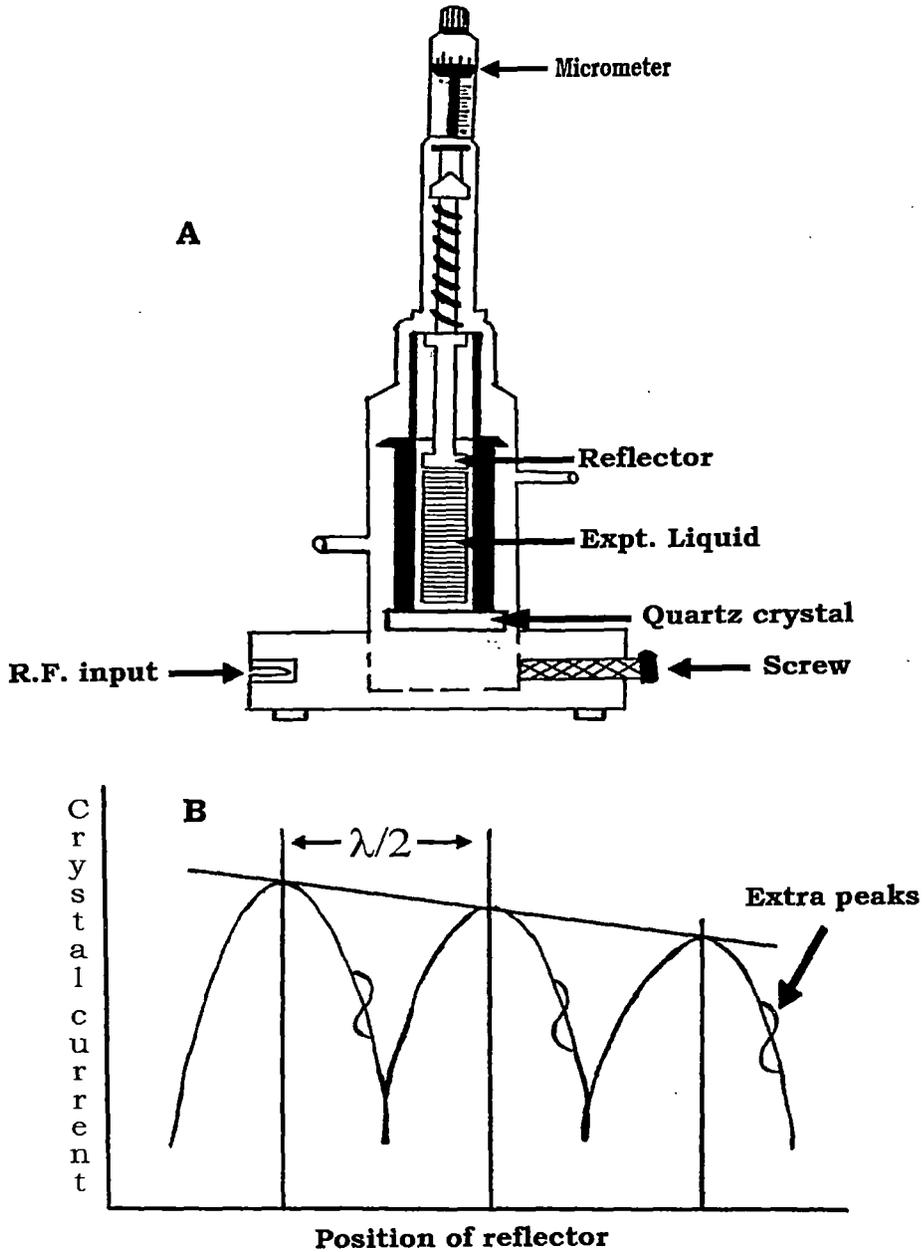


Figure 2. A Multi-frequency Ultrasonic Interferometer- (A) Cross-section of the measuring cell and (B) Position of reflector vs. crystal current.

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3.2.4. *Measurement of Conductance*

Systronics Conductivity meter- 306 is used for measuring specific conductivity of electrolytic solutions. It is a microprocessor based instrument and can provide both automatic and manual temperature compensation. The instrument shows the conductivity of the solution under test at the existing temperature or with 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, CD-10 with a cell constant of $1.0 \pm 10\% \text{ cm}^{-1}$. The instrument was standardized using 0.1(M) KCl solution. The cell was calibrated by the method of Lind and co-workers.⁴⁰ The measurements were made in a thermostatic water bath maintained at the required temperature with an accuracy of $\pm 0.01 \text{ K}$, described earlier.

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.

Figure 3 on next page shows the Systronics Conductivity meter- 306 i.e. (A) Isometric view and (B) Block diagram of the instrument.

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