

CHAPTER-3

3.1. Source and Purification of the Chemicals used:

3.1.1. Solvents:

1,3-Dioxolane (C₃H₆O₂, M.W. 74.08), Merck /SD, was heated under reflux with PbO₂ for 2 hrs, then cooled and filtered. After adding xylene to the filtrate, the mixture was fractionally distilled.^{1,2} The solvent obtained after purification had a boiling point of 348 K / 760 mm, a density of 1057.1 kg.m⁻³ and a coefficient of viscosity of 0.531 mPa.s at 298.15 K.

1,4-Dioxane (C₄H₈O₂, M.W. 88.11), Merck, India, was kept several days over potassium hydroxide (KOH), followed by refluxing over excess of sodium for 12 hours.^{2,3} Finally, it was distilled from sodium. The pure liquid had a boiling point of 375 K/760 mm, density of 1026.5 kg.m⁻³ and a coefficient of viscosity of 1.196 mPa.s at 298.15 K.

N, N-Dimethylformamide (C₃H₇NO, M.W. 73.10), Merck, India, was mixed with 10% (by volume) benzene, and the azeotrope was distilled off under atmospheric pressure at about 353 K. The product was dried over silica gel and distilled at reduced pressure, with the middle fraction being collected. The purified solvents was stored over P₂O₅ in a desiccator before use.⁴ The solvent had boiling point of 426 K/760 mm and 349 K/39 mm, a density of 944.2 kg.m⁻³ and a coefficient of viscosity 0.8016 mPa.s at 298.15 K.

Tetrahydrofuran (C₄H₈O, M.W. 72.11), Merck /SRL, was kept for several days over KOH, refluxed for 24 h, and distilled over LiAlH₄.^{2,5} The boiling point (66 °C), density (0.8807 g/cm³), and viscosity ($\eta_0 = 0.4630$ mPa s) at 298.15 K. The specific conductance of THF was $\approx 0.81 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ at 28.15 K. The purity of the solvent finally obtained was >99.0 %.

methanol (CH₄O); ethanol (C₂H₆O); 1-propanol (C₃H₈O); 1-butanol (C₄H₁₀O); 1-pentanol (C₅H₁₂O); 1-hexanol (C₆H₁₄O); 1-heptanol (C₇H₁₆O); 1-octanol (C₈H₁₈O); 1-nonanol (C₉H₂₀O) and 1-decanol (C₁₀H₂₂O) (Merck/ S. D. Fine Chemicals, Urasol grade) were dried over 4Å molecular sieves and then distilled fractionally. Middle fraction was collected and redistilled⁶.

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Benzene (S. D. Fine Chemicals, purity > 99%) was purified by means of a simple distillation technique with the first and last 20% of the distillate being discarded and finally the density and viscosity value compared with the literature.⁷

Extrapure grade 2-methoxyethanol, 2-ethoxy- ethanol, acetonitrile, 1,2-dimethoxyethane, and dimethylsulfoxide procured from S.d.fine-Chem /Merck/SRL. 2-ethoxy- ethanol was purified as described in the literature.⁸ 2-Methoxyethanol was dried with potassium carbonate and distilled twice in an all-glass distillation set immediately before use, and the middle fraction was collected.⁹ Acetonitrile was distilled from P₂O₅ and then from CaH₂ in an all-glass distillation apparatus.¹⁰ The middle fraction was collected. 1,2-Dimethoxyethane was purified by double-fractional distillation over LiAlH₄ to eliminate traces of acids, peroxides, and water, and the middle portion was collected for the preparation of mixtures.¹¹ Dimethylsulfoxide was purified according to the standard procedures.^{2,12} All solvents were stored over 3 Å molecular sieves for 3 days before use. The purity of the purified liquids was ascertained by GLC and also by comparing experimental values of densities, viscosities, and ultrasonic speeds of sound with their literature values.^{2,9-14}

Water was first deionized and then distilled in an all glass distilling set along with alkaline KMnO₄ solution to remove any organic matter⁹ therein. The doubly distilled water was finally distilled using an all glass distilling set. Precautions were taken to prevent contamination from CO₂ and other impurities. The triply distilled water had specific conductance less than 1×10^{-6} S.cm⁻¹.

Densities and viscosities of the purified solvents were in good agreement with the literature values.²⁻¹⁵ and are listed in the respective chapters. The purity of most of the solvents finally obtained was better than 99.5 %.

3.1.2. Mixed solvents:

The mixed solvents containing 10, 20, 30 mass % of tetrahydrofuran + H₂O mixtures and 10, 20, 30 mass % of 1,3-dioxolane + H₂O mixtures were prepared accurately by mixing the requisite volume of the respective cyclic ethers and H₂O with earlier conversion of required mass of the respective solvents to volume by using experimental densities of the solvents at experimental temperature.

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Besides these solvent mixtures, other solvent mixtures includes with monoalkanols +2 Methoxyethanol, tetrahydrofuran, 1,3 dioxolane ;methanol+1,4 dioxane ;Acetonitrile + dimethylsulfoxide; N,N-dimethylformamide +benzene, 1,3 dioxolane, 1,4 dioxane, tetrahydrofuran, 1,2-dimethoxyethane, di-isopropylether, diethylether, 2-methoxyethanol and 2-ethoxyethanol have been used for my research studies. The physical properties of different pure and mixed solvents have been presented in the respective chapters.

3.1.3. Solutes:

Tetraalkylammonium salts viz. tetrapentylammonium chloride (Pen_4NCl), tetrahexylammonium chloride (Hex_4NCl), tetraheptylammonium chloride (Hp_4NCl) and tetraoctylammonium chloride (Oct_4NCl), were of Fluka's purum or puriss grade and purified by dissolving in mixed alcohol medium and recrystallised from solvent ether medium. After filtration, the salts were dried in an oven for few hours. The crystallised salts were dried in vacuum. The salts were stored in glass bottles in darkened desiccator over fused CaCl_2 .^{6,16}

Alkali metal halides were of Purum or Puriss grade [Loba Chemie/ S.D.Fine.Chem/ Merck/ Qualigens Fine Chem./ Aldrich Chem] and were used as such after drying over CaO for 48 hours and were purified in the manner given in the literature.^{17,18,19,20}

Resorcinol (S.D.Fine.Chem ,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 procedure²¹.

Nicotinamide was purchased from ACROS Organics company and used as such. Its mass purity as supplied is 98%.

Ammonium thiocyanate, Sodium thiocyanate and Potassium thiocyanate salts (all A.R., B.D. H.) were purified by recrystallization twice from conductivity water. The samples were dried in vacuum and stored over P_2O_5 under vacuum.

Ammonium and Sodium acetate (Riedel A.R) were used as received. Lithium and Potassium acetates were purified by the reported procedures.²¹ The salts were dried and stored in vacuum desiccator.

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The purity of the solutes finally obtained was better than 99.0 % as checked by melting point determination.

3.2. Experimental Methods:

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, 318.15 and 323.15 K with doubly distilled water and benzene using density and viscosity values from the literature.^{22,23} 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.

The temperature of the thermostatic water bath 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.²⁴ 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.^{3, 25-28}

3.2.2. Measurement of Viscosity:

The kinematics viscosities were measured by means of a suspended-level Ubbelohde²⁹ 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

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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 kinematics 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 1.9602×10^{-3} and 4.2019 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, based on our work on several pure liquids, was $\pm 2 \times 10^{-4}$ mPa.s.

3.2.3. Measurement of Ultrasonic Speed:

Ultrasonic speeds were measured, with an accuracy of 0.3 %, using a single crystal variable-path ultrasonic interferometer³⁰ (Model M-81, Mittal Enterprise, New Delhi) operating at 2 MHz, which was calibrated with water, methanol and benzene at the experimental temperature. The temperature stability was maintained within ± 0.01 K of the desired temperature 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

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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.

3.2.4. Measurement of Conductance:

Systronic 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.

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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.³¹ The measurements were made in a thermostatic water bath maintained at the required temperature with an accuracy of $\pm 0.01 \text{ K}$.

Several solutions were prepared by mass accurate to $\pm 0.01 \text{ mg}$ with the aid of a Mettler electronic analytical balance (AG 285, Switzerland) 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.

3.2.5 Spectroscopy

Infrared spectra was recorded on a 8300 FTIR spectrometer (Shimadzu-Japan) with a resolution of $\pm 0.25 \text{ cm}^{-1}$ in the region $4000\text{-}400 \text{ cm}^{-1}$ at room temperature (25°C) with 49-54 % humidity. This KBr optics based instrument records data in different modes (KBr Pellets, Nujol mull, non-aqueous solutions). The Spectrometer is equipped with Michelson interferometer, single beam optics, Ge/KBr beam splitter, ceramic beam source, a high sensitivity pyroelectric detector (DLATGS) and He-Ne laser for data sampling. The spectra was properly normalized in order to take into account the effective number of absorbers.

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References:

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