

A.3: Experimental Section

A.3.1. Source and Purification of the Chemicals used:

A.3.1.1. Solvents:

1,4-Dioxane ($C_4H_8O_2$, M.W. 88.11), Merck, India, was kept several days over potassium hydroxide (KOH), followed by refluxing over excess of sodium for 12 hours^{1,2} Finally, it was distilled from sodium. The pure liquid had a boiling point of 375 K/760 mm, density of $1026.5 \text{ kg}\cdot\text{m}^{-3}$ and a coefficient of viscosity of $1.196 \text{ mPa}\cdot\text{s}$ at 298.15 K.

1,3-Dioxolane ($C_3H_6O_2$, M.W. 74.08), Merck, India, was heated under reflux with PbO_2 for 2 hrs, then cooled and filtered. After adding xylene to the filtrate, the mixture was fractionally distilled^{1,3}. The solvent obtained after purification had a boiling point of 348 K / 760 mm, a density of $1057.1 \text{ kg}\cdot\text{m}^{-3}$ and a coefficient of viscosity of $0.531 \text{ mPa}\cdot\text{s}$ at 298.15 K.

Tetrahydrofuran (C_4H_8O , M.W. 72.11), Merck, India, was kept for several days over KOH, refluxed for 24 h, and distilled over $LiAlH_4$ ^{1,4} The boiling point (66°C), density ($0.8807 \text{ g}/\text{cm}^3$), and viscosity ($\eta_0 = 0.4630 \text{ mPa}\cdot\text{s}$) 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 $>99.0\%$.

N, N-Dimethylformamide (C_3H_7NO , 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 P_2O_5 in a desiccator before use⁵. The solvent had boiling point of 426 K/760 mm and 349 K/39 mm, a density of $944.2 \text{ kg}\cdot\text{m}^{-3}$ and a coefficient of viscosity $0.8016 \text{ mPa}\cdot\text{s}$ at 298.15 K.

The Alcohols used for the experimental purposes i.e. methanol (CH_3OH , M.W. 32.04), ethanol (C_2H_5OH , M.W. 46.07), 1-propanol (C_3H_7OH , M.W.60), 2-propanol (C_3H_7OH , M.W.60) 1-butanol (C_4H_9OH M.W. 74.12), 2-butanol (C_4H_9OH M.W. 74.12) were dried over 4\AA molecular sieves and then distilled fractionally. Middle fraction was collected and redistilled⁶.

n-Amyl alcohol ($C_5H_{11}OH$, M.W. 88.15, A. R. grade, purity $> 99\%$) and iso-amyl alcohol ($C_5H_{11}OH$, M.W. 88.15, A. R. grade, purity $> 99\%$), Merck, India, were dried with anhydrous K_2CO_3 and distilled. The middle fractions for both the liquids were collected and kept free from humidity with 3\AA molecular sieves.⁷

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Dimethylsulphoxide solvent were stored over 3 Å molecular sieves for 3 days before use. It is then refluxed for 4hr over CaO The purity of the purified liquid was ascertained by GLC and also by comparing experimental values of densities, viscosities, and ultrasonic speeds of sound with their literature values^{1,8-13}.

Acetonitrile (CH₃CN, M.W. 41.05), S. D. Fine Chemical Limited, Mumbai, India, was distilled with P₂O₅ and then redistilled over CaH₂ in an all-glass distillation apparatus. The middle fraction was collected for us⁹.

Acrylonitrile ,purchased from S.D. Fine Chemicals Ltd., Mumbai, India, was washed with dilute H₂SO₄, then with dilute Na₂CO₃ and water, and again dried over anhydrous CaCl₂ and distilled fractionally¹⁴.

To prevent oxidation benzaldehyde usually contains additives such as catechol .After filtration benzaldehyde was washed with 10 % Na₂CO₃ (until no more CO₂ evolved), then with saturated Na₂SO₃ and water, followed by drying with CaCl₂¹⁵.

Anisaldehyde was washed with NaHCO₃, then with water, dried with anhydrous MgSO₄, and distilled under reduced pressure under N₂¹⁵

Cinnamaldehyde was crystallized from benzene and dried at 60 °C under vacuum¹⁵. The gas-liquid chromatography (GLC) analyses of these liquids indicated a mole fraction purity of > 99.0 %. The purity of the liquids was also checked by measuring their densities and viscosities at 298.15 K and was in reasonable agreement with the literature values as shown in Table 1.

Cyclohexylamine (Merck, India), Cyclohexanone, Butylacetate, Butylamine, *tert*-Butylamine and Butanone (S.D. Fine Chemicals, Analytical Reagent, purity > 99 %) were used without further purification.

2-butoxyethanol (S. D. Fine Chemicals, AR, India) were purified as described in the literature¹⁶ The pure chemicals were stored over activated 4 Å molecular sieves to reduce water content before use. The chemicals after purification were 99.8% pure and their purity was ascertained by GLC and also by comparing experimental values of densities and viscosities with those reported in the literature¹⁶⁻²¹ when available, as presented in Table 1.

Water was first deionized and then distilled in an all glass distilling set along with alkaline KMnO₄ solution to remove any organic matter⁸ therein. The doubly distilled water was finally distilled using an all glass distilling set. Precautions were taken to prevent contamination

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from CO₂ and other impurities. The triply distilled water had specific conductance less than $1 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$.

Densities and viscosities of the purified solvents were in good agreement with the literature values¹⁻¹⁶ and are listed in the respective chapters. The purity of most of the solvents finally obtained was better than 99.5 %.

A.3.1.2. Mixed solvents:

The research work has been carried out with binary or ternary solvent systems with acrylonitrile, tetrahydrofuran, cyclohexylamine, cyclohexanone, dimethylsulphoxide, acetonitrile or 1,3-dioxolane as primary solvents with some polar, weakly polar and non-polar solvents as well as with some solutes.

For the preparation of mixed binary and ternary mixtures, pure components were taken separately in glass Stoppard bottles and thermo stated at the desired temperature for sufficient time. When the thermal equilibrium was ensured, the required volumes of each component were transferred in a different bottle which was already cleaned and dried thoroughly. Conversion of required mass of the respective solvents to volume was accomplished by using experimental densities of the solvents at experimental temperature. It was then Stoppard and the mixed contents were shaken well before use. While preparing different binaries and ternaries care was taken to ensure that the same procedure was adopted throughout the entire work. The physical properties of different pure and mixed solvents have been presented in the respective chapters. The following different binary and ternary solvent mixtures have been prepared and used for my research studies.

Binary mixtures studied:

Acrylonitrile (1) + Cinnamaldehyde (2)

Acrylonitrile (1) + Anisaldehyde (2)

Acrylonitrile (1) + Benzaldehyde (2)

Cyclohexylamine (1) + Butylamine (2)

Cyclohexylamine (1) + *tert*-butylamine (2)

Cyclohexylamine (1) + Butanone(2)

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Cyclohexylamine (1) + Butylacetate (2)
Cyclohexylamine (1) + 2-butoxyethanol (2)
Cyclohexanone (1) + Butylamine (2)
Cyclohexanone (1) + *tert*-butylamine (2)
Cyclohexanone (1) + Butanone(2)
Cyclohexanone (1) + Butylacetate (2)
Cyclohexanone (1) + 2-butoxyethanol (2)

Ternary mixtures studied:

1,4-dioxane (1) + Dimethylformamide(2) + Methanol (3)
1,4-dioxane (1) + Dimethylformamide(2) + Ethanol (3)
1,4-dioxane (1) + Dimethylformamide(2) + 1-propanol (3)
1,4-dioxane (1) + Dimethylformamide(2) + 2-propannol (3)
1,4-dioxane (1) + Dimethylformamide(2) + 1-butanol (3)
1,4-dioxane (1) + Dimethylformamide(2) + 2-butanol (3)
1,4-dioxane (1) + Dimethylformamide(2) + 1-pentanol (3)
1,4-dioxane (1) + Dimethylformamide(2) + *iso*-amylalcohol (3)

Solute-solute / ion-ion and solute-solvent / ion-solvent interactions studied in the following mixed solutions:

Catechol(1) + Water (2) + Glycine (3)
Catechol(1) + Water (2) + DL-alanine (3)
Catechol(1) + Water (2) + L-valine (3)
Catechol(1) + Water (2) + L-leucine (3)

Tetrahydrofuran (1) + 1,4-dioxane (2) + Tetrapentylammonium Iodide(3)
Tetrahydrofuran(1) + 1,4-dioxane (2) + Tetrahexylammonium Iodide(3)
Tetrahydrofuran(1) + 1,4-dioxane (2) + Tetraheptylammonium Iodide(3)

Tetrabutylammonium bromide(1) + water (2) + Ascorbic acid (3)

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Dimethylsulphoxide (1) + Acetonitrile (2) + Lithium bromide (3)

Dimethylsulphoxide (1) + Acetonitrile (2) + Sodium bromide (3)

Dimethylsulphoxide (1) + Acetonitrile (2) + Sodium Iodide(3)

Dimethylsulphoxide (1) + Acetonitrile (2) + Potassium Iodide (3)

Dimethylsulphoxide (1) + Acetonitrile (2) + Tetrabutylammonium bromide (3)

Dimethylsulphoxide (1) + Acetonitrile (2) + Sodium tetraphenyl borate (3)

Dimethylsulphoxide (1) + Acetonitrile (2) + Lithium chloride (3)

1,3-dioxolane (1) + Water (2) + Oxalic acid (3)

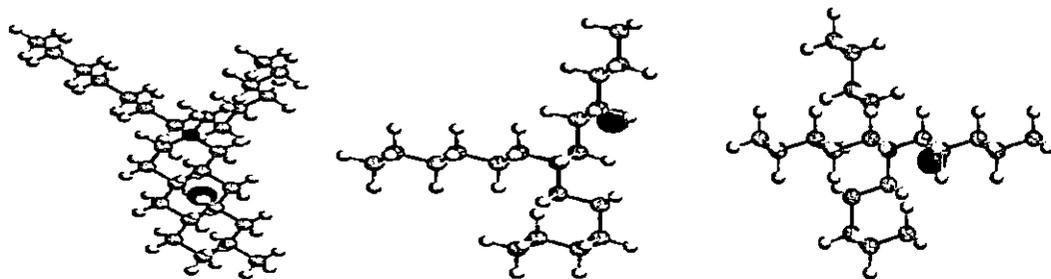
1,3-dioxolane (1) + Water (2) + Sodium oxalate (3)

1,3-dioxolane (1) + Water (2) + Potassium oxalate (3)

1,3-dioxolane (1) + Water (2) + Ammonium oxalate (3)

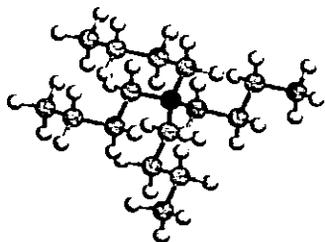
A.3.1.3. Solutes:

Tetraalkylammonium salts viz. tetrapentylammonium iodide (Pen_4NI), tetrahexylammonium iodide (Hex_4NI), tetraheptylammonium iodide (Hp_4NI), tetrabutylammonium bromide (Bu_4NBr), 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 ^{22,23}

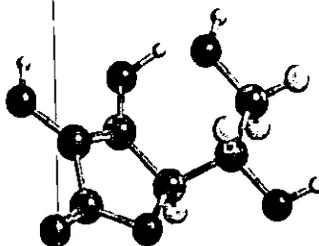


Tetraheptylammoniumiodide Tetrahexylammoniumiodide Tetraheptylammoniumiodide

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Tetrabutylammoniumbromide

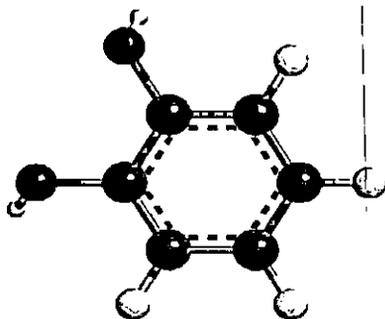


Ascorbic acid

Ascorbic acid was recrystallised twice from aqueous ethanol solution and dried under vacuum at $T=348$ K for 6 hr. Thereafter, they were stored over P_2O_5 in a desiccator before use⁷.

Sodium tetraphenylborate ($NaB(C_6H_5)_4$), M.W. 342.23), procured from Fluka puram, was recrystallized three times from acetone and dried under vacuum at 353.15 K for 72 hours.

Catechol (S.D.Fine.Chem, A.R.,purity 99%) catechol was purified by repeated crystallization from mixture of chloroform-methanol. The sample was dissolved in chloroform in hot condition, filtered and to the filtrate dried & distilled methanol was added dropwise. Fine plat like crystal separated and recovered by rapid filtration & ready for use. Deionized, doubly distilled, degassed water with a specific conductance of less than $10^{-6} \Omega \cdot cm^{-1}$ was used for all of the measurements. The purity of the solvents was ascertained by GLC.

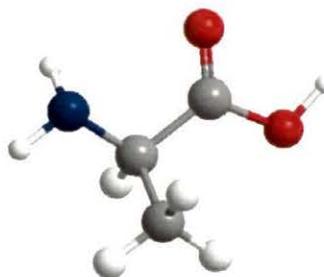


Catechol

The amino acids glycine (S.D. Fine Chemicals, India, Purity>99%), DL-alanine (S.D. Fine Chemicals, India, Purity > 98.5%), L-valine (S.D. Fine Chemicals, India, Purity > 99%), and L-leucine (Thomas Baker, India, Purity>98%) were were recrystallised from methanol-water mixture and dried at 373.15 K for 12 h in an infrared drier and then in vacuo over P_2O_5 at room

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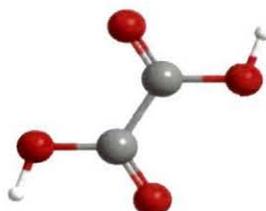
temperature²². The purity of the solutes finally obtained was better than 99.0 % as checked by melting point determination.



Glycine

Metal salts like lithium iodide, lithium chloride, lithium bromide, sodium iodide, potassium iodide were obtained from (Loba Chemie/S.D.Fine/E.Merck,India/Aldrich Chem) and were used as such after drying over CaO for 48 hours and purified in the manner given in the literature^{1,3,7}.

Oxalic acid, ammonium oxalate, sodium oxalate and potassium oxalate, all of Analytical Reagent grade, were used as such only after drying over P₂O₅ in a desiccator for more than 24 h. The reagents were always placed in the desiccators over P₂O₅ to keep them in dry atmosphere²².



Oxalic acid

A.3.2. Experimental Methods:

A.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

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benzene using density and viscosity values from the literature^{24,25}. 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.



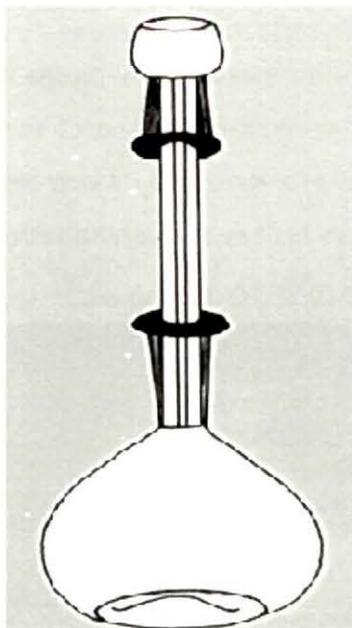
Mettler Toledo Digital Electronic Balance



Rotary Vacuum Flash Evaporator

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 bridge²⁶. 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^{2,27-30}

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An Ostwald- Sprengel-type pycnometer.

The density was also measured by the density meter (Anton Paar DMA 4500M GmbH Austria-Europe). The accuracy of the density measurement was $\pm 5 \times 10^{-5} \text{ g}\cdot\text{cm}^{-3}$



Density Meter

Anton Paar DMA 4500M GmbH Austria-Europe

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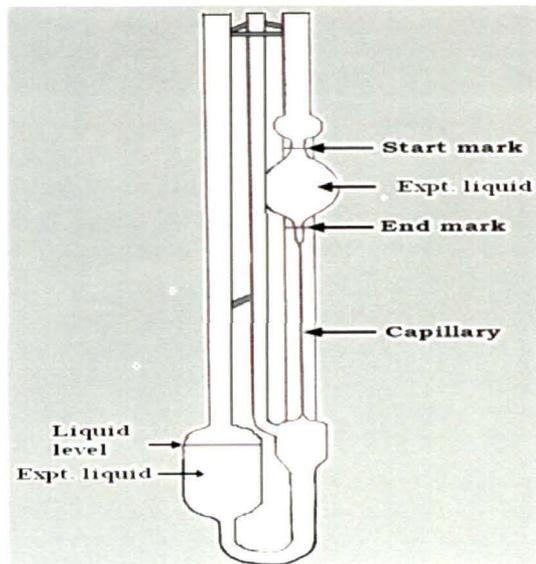
A.3.2.2. Measurement of Viscosity:

The kinematics viscosities were measured by means of a suspended-level Ubbelohde³¹ 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.



Thermostat Water Bath

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.



A suspended-level Ubbelohde viscometer

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

$$\nu = Kt - \frac{L}{t} \quad (1)$$

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

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:

$$\eta_r = \frac{\eta}{\eta_0} = \frac{\rho t}{\rho_0 t_0} \quad (3)$$

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.

A.3.2.3. Measurement of Ultrasonic Speed:

Ultrasonic speeds were measured, with an accuracy of 0.3 %, using a single crystal variable-path ultrasonic interferometer³² (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 electrical reaction on the generator driving the quartz crystal and the anode current of the generator becomes a maximum.

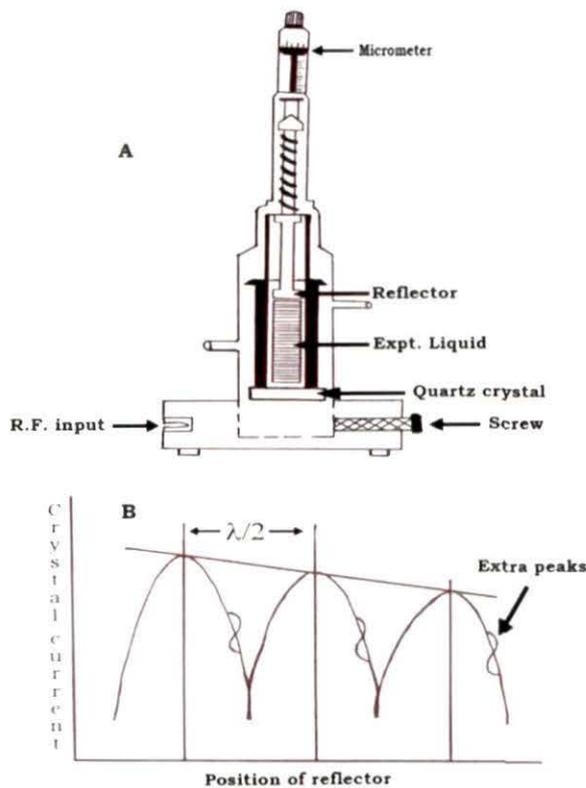
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Multifrequency Ultrasonic Interferometer

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:

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



(A) Cross-section of the measuring cell of a Multifrequency Ultrasonic Interferometer and
(B) Position of reflector vs. crystal current

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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.

A.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.

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 instru. was standardized using 0.1 (M) KCl solution. The cell was calibrated by the method of Lind and co-workers³³. The measurements were made in a thermostatic water bath maintained at the required temperature with an accuracy of $\pm 0.01 \text{ K}$.

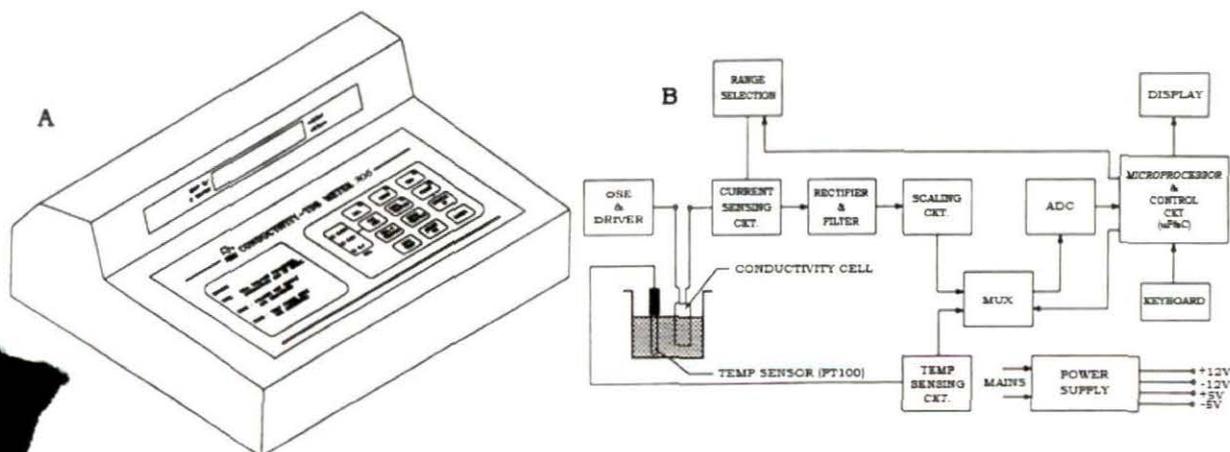
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Several solutions were prepared by mass accurate to ± 0.01 mg with the aid of a Mettler electronic analytical balance (AG 285, Switzerland) and runs were performed to ensure the reproducibility of the results. Due correction was made for the specific conductance of the solvents at desired temperatures.



Systronic-308 Conductivity Bridge (FTIR SHIMADZU)

The following figure shows the Systronic Conductivity meter- 308, i.e., (A) Isometric view and (B) Block diagram of the instrument



The Systronic Conductivity meter 308- (A) Isometric view and (B) Block diagram of the instrument.

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