CHAPTER III

3.1. Source and Purification of the Chemicals used

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, a density of 1026.5 kg.m^{-3} and a coefficient of viscosity of 1.196 mPa.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.[2,3] 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.

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 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.

Butylamine ($C_4H_{11}N$, M.W73.14), S. D. Fine Chem, minimum assay GLC, 98% was stored over sodium hydroxide pellets for several days and fractionally distilled twice. [5]

Alkyl acetates like Methyl acetate ($C_3H_6O_2$, M.W74.08),, ethyl acetate ($C_4H_8O_2$, M.W 88.11), butyl acetate ($C_6H_{12}O_2$, M.W116.16), and iso-amyl acetate ($C_7H_{14}O_2$, M.W130.19) were of A. R. grade, purity>99% and procured from S. D. Fine Chemicals, India. Methyl acetate was washed with saturated solution of NaCl, dried with anhydrous $MgCl_2$, and then distilled. Ethyl acetate was dried over K_2CO_3, filtered, and distilled, and the first and the last portions of the distillate were discarded. The entire middle fraction was then distilled over P_2O_5. Butyl acetate and iso-amyl acetate were purified by drying over $CaCO_3$ overnight, filtered, and freshly distilled.

The Alcohols used for the experimental purposes i.e. methanol (MeOH, CH_3OH, M.W. 32.04), ethanol (EtOH, C_2H_5OH, M.W. 46.07), 1-butanol (1-BuOH, C_4H_9OH, M.W. 74.12), 2-butanol (2-BuOH, C_4H_9OH, M.W. 74.12), iso-butanol (i-BuOH, C_4H_9OH, M.W. 74.12) and t-butanol (t-BuOH, C_4H_9OH, M.W. 74.12) (Merck, India, Urasol grade) were dried over 4Å molecular sieves and then distilled fractionally. Middle fraction was collected and redistilled.

2-methoxy-, 2-ethoxy- and 2-butoxyethanol (S. D. Fine Chemicals, AR, India) were purified as described in the literature.[6] Glycerol (G.R.E. Merck, India, >99.5%) was purified as described earlier.[7]

2-butanone, isopropylamine, cyclohexylamine and diethylamine were procured from Merck, India and were used as purchased. However, they were stored over activated 4Å molecular sieves to reduce water content before use.

Water was first deionized and then distilled in an all glass distilling set along with alkaline $KMnO_4$ solution to remove any organic matter[8] therein. The doubly distilled water was 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 1×10^{-6} S.cm^{-1}.

Densities and viscosities of the purified solvents were in good agreement with the literature values.[2-11] 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, 40, 60, 80 mass % of 1,4-dioxane + H_2O mixtures and 10, 20, 30 mass % of 1,3-dioxolane or glycerol + H_2O mixtures were prepared accurately by mixing the requisite volume of the respective cyclic ethers and H_2O with earlier conversion of required mass of the respective solvents to volume by using experimental densities of the solvents at experimental temperature.

Besides these solvent mixtures, other solvent mixtures includes 1,4-dioxane/1,3-dioxolane + butyl acetate, + butyric acid, + butylamine, + 2-butanone and butylamine/DMF + alkyl acetates; 2-butanone + alkyloxy substituted ethanols, + isopropylamine, + cyclohexylamine, + diethylamine and DMF + isomeric butanols etc. 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. tetramethylammonium chloride (Me_4NCl, M.W. 109.60), tetramethylammonium iodide (Me_4NI, M.W. 201.05), tetraethylammonium bromide (Et_4NBr, M.W. 210.16), tetrapropylammonium bromide (Pr_4NBr, M.W. 266.27), tetrabutylammonium bromide (Bu_4NBr, M.W. 322.37), and tetrabutylammonium iodide (Bu_4NI, M.W. 369.38) were of A. R. grade (Aldrich) 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 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 $CaCl_2$.

Ammonium fluoride (NH_4F, M.W. 37.04), ammonium chloride (NH_4Cl, M.W. 53.50), and ammonium bromide (NH_4Br, M.W. 97.95) were of A. R. grade (SD fine chemicals) and were dried at about 80-100° C in a vacuum oven for 48 hours before use.

Potassium metal salts (KCl, KBr and KI) were of puris or purum grade (Fluka), quoted as 99.5% pure and were purified as described earlier.[12, 13]

Sodium molybdate ($Na_2MoO_4.2H_2O$, M. W. 241.95) was of A. R. grade (NICE, India) and purified by recrystallising twice from conductivity water and was dried in a vacuum desiccator over P_2O_5 for 24 hours before use.

The amino acids glycine (Analar, BDH, Purity>99%), L-alanine (S.D. Fine Chemicals, India, Purity>98.5%), L-valine (Loba Chemie, India, Purity>99%), and Tetramethylammonium iodide (Thomas Baker, India, Purity>98%) were were recrystalised 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 temperature.

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 and 318.15 K with doubly distilled water and benzene using density and viscosity values from the literature.[14, 15] 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 ± 3 × 10⁻⁴ g.cm⁻³. Figure 1 shows an Ostwald-Sprengel type pycnometer (Single arm) used in our works.
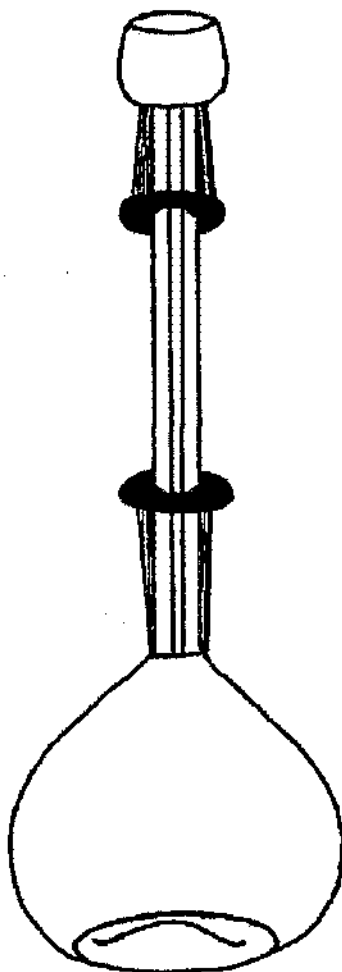
Figure 1. An Ostwald- Sprengel type pycnometer.

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.[16] 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.[1, 17-20]

3.2.2. Measurement of Viscosity

The kinematic viscosities were measured by means of a suspended-level Ubbelohde[21] 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 ± 0.1s. 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 ware measured a number of times and the average of the readings was taken into account. The kinematic viscosity (v) and the absolute viscosity (η) are given by the following equations.

$$v = Kt - L/t \tag{1}$$

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

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:

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

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. Figure 2 shows a suspended-level Ubbelohde viscometer used in our works.
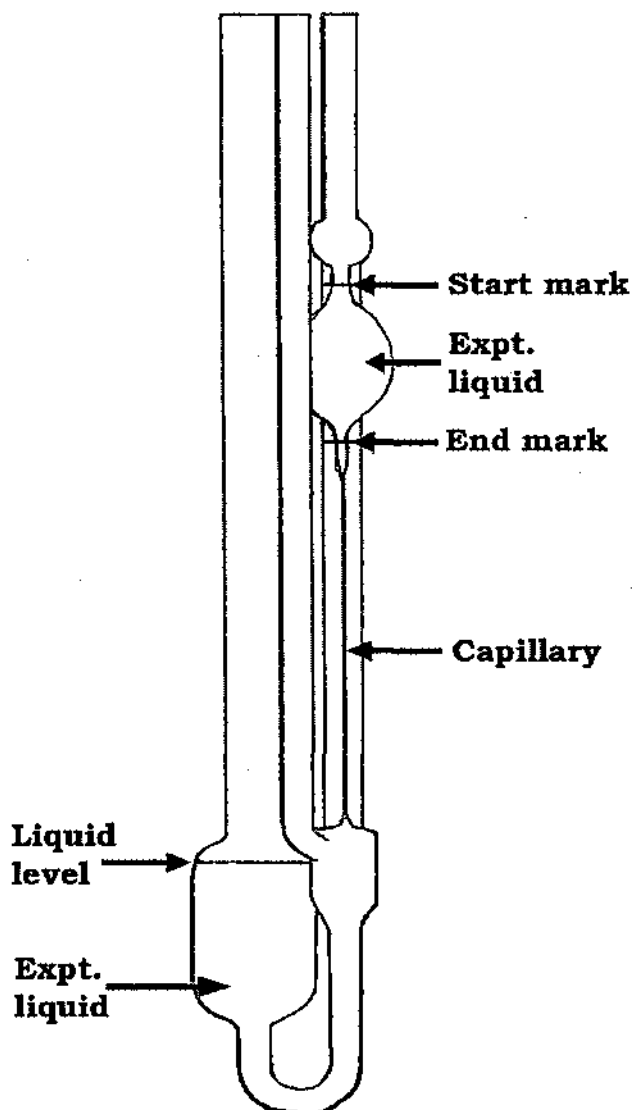
Figure 2. A suspended-level Ubbelohde viscometer.

3.2.3. Measurement of Ultrasonic Speed

Ultrasonic speeds were measured, with an accuracy of 0.3 %, using a single-crystal variable-path ultrasonic interferometer[22] (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.

Experimental Section

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:

$$u = \lambda \times f \tag{4}$$

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.

$$d = n \times \lambda/2 \tag{5}$$

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

$$K_S = 1/(u^2 \rho) \tag{6}$$

where ρ is the density of the experimental liquid.

In figure 3- (A) Cross-section of the measuring cell of a Multifrequency Ultrasonic Interferometer and (B) Position of reflector vs. crystal current are depicted.
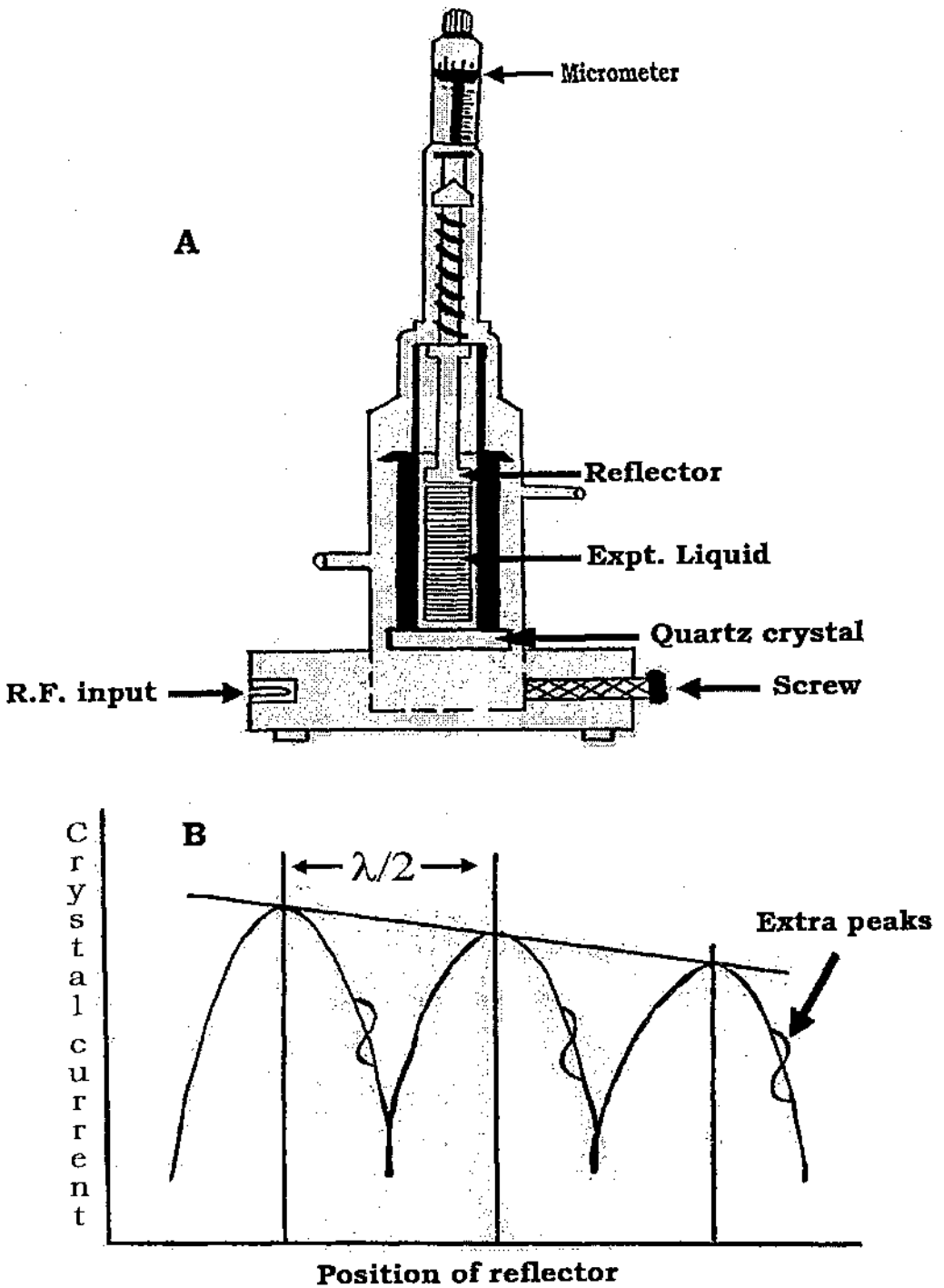
Figure 3. (A) Cross-section of the measuring cell of A Multi-frequency Ultrasonic Interferometer, (B) Position of reflector vs. crystal current.

However, the extra peaks (Figure 3B) in between minima and maxima occurs due to a number of reasons, but these do not effect the value of $\lambda/2$.

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 $1.0 \pm 10\%$ cm^{-1}. The instrument was standardized using 0.1 (M) KCl solution. The cell was calibrated by the method of Lind and co-workers.[23] The measurements were made in a thermostatic water bath maintained at the required temperature with an accuracy of ± 0.01 K.

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.

Figure 4 shows the Systronic Conductivity meter- 306 i.e. (a) Isometric view and (b) Block diagram of the instrument.
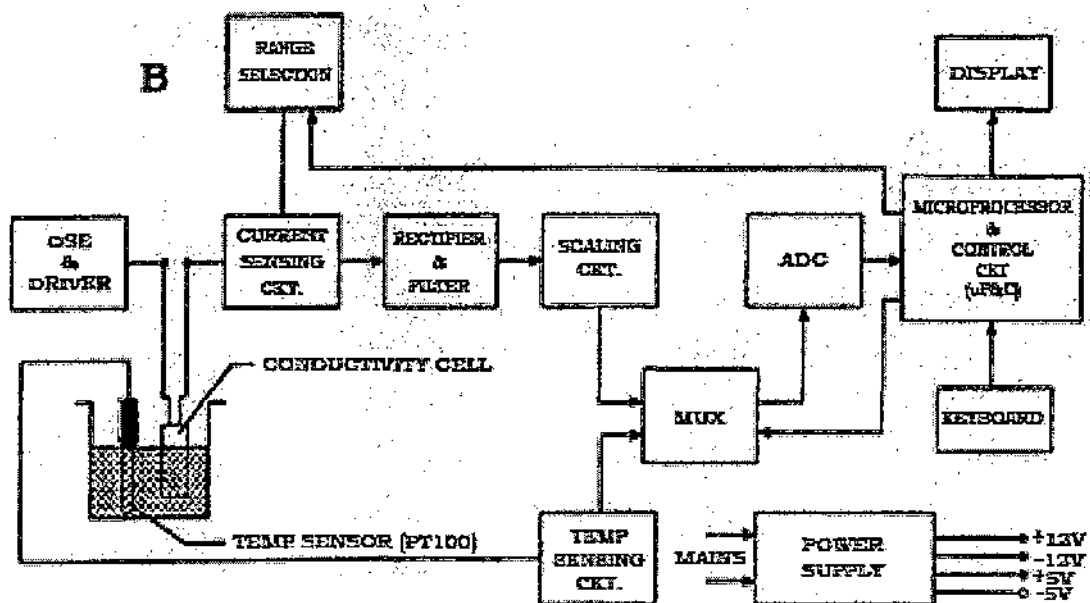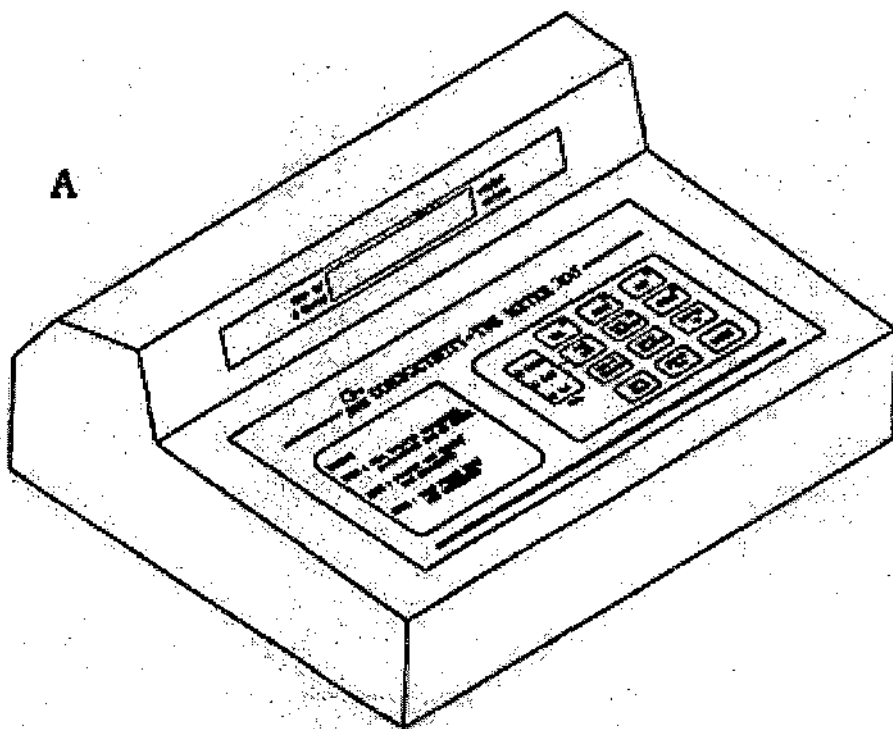
Figure 4. The Systronic Conductivity meter 306- (A) Isometric view and (B) Block diagram of the instrument.

References

[1]   B. Das, M.N. Roy, D.K.Hazra, Ind. J. Chem. Tech., 1 (1994) 93.

[2]   A. K. Covington, T. Dickinson, *Physical Chemistry of Organic Solvent Systems*, Plenum, New York, (1973).

[3]   J. A. Riddick, W. B. Bunger, T. K. Sakano, *Organic Solvents: Physical Properties and Methods of Purification*, Wiley, New York, (1986).

[4]   Y. Zhao, J. Wang, X. Xuan, J. Lu, J. Chem. Eng. Data., 45 (2000) 440.

[5]   T. M. Letcher, J. Chem. Thermodyn., 4 (1972) 159.

[6]   N. V. sastry, S. . Patel, Int. J. Thermophys., 21 (2000) 1153.

[7]   M. M. Emara, H. A. Shehata, J. Chin. Chem. Soc., 35 (1988) 337.

[8]   Z. Yan, J. Wang, J. Lu, J. Chem. Eng. Data., 1 (2001) 217.

[9]   T. Timmermans, *Physico Chemical Constants of Pure organic Compounds*, Elsevier, Amsterdam, 1, (1950).

[10] J. V. Herraez, R. Belda, J. Soln. Chem., 33 (2004) 117.

[11] M. N. Roy, A. Jha, R. Dey, J. Chem. Eng. Data., 46 (2001) 1327.

[12] D. Nandi, D. K. hazra, J. Chem. Soc. Faraday Trans 1., 85 (1989) 1531.

[13] M. N. Roy, D. Nandi, D. K. Hazra, J. Ind. Chem. Soc., 70 (1993) 121.

[14] K. N. Marsh, "*Recommended Reference Materials for the Realisation of Physicochemical Properties*", Blackwell Scientific Publications, Oxford, U. K., (1987).

[15] J. A. Dean, "*Lange's Handbook of Chemistry*", 11th ed., McGraw-Hill Book Company, New York, (1973).

[16] D. Dasgupta, S. Das, D. K. Hazra. J. Chem. Soc. Faraday Trans I., 84 (1988) 1057.

[17] P. S. Nikam, M. Hosan, J. Chem. Eng. Data., 33 (1988) 165.

[18] R. D. Peralta, R. Infante, G. Cortez, G. Cadenas, J. Wisniak, Int. J. Thermophys., 24 (2003) 1061.

[19] S. Martin Contreras, J. Chem. Eng. Data., 46 (2001) 1149.

[20] R. Francesconi, F. Comelli, J. Chem. Eng. Data., 40 (1995) 31.

[21] J. R. Suindells, J. R. Coe Jr., T. B. Godfray. J. Res. Natd. Bus. Stand., 48 (1952) 1.

[22] M. N. Roy, A. Jha, A. Choudhury, J. Chem. Eng. Data., 49 (2004) 291.

[23] J. E. Lind Jr., J. J. Zwolenik, R. M. Fuoss, J. Chem. Soc. Faraday Trans I., 81 (1959) 1557.