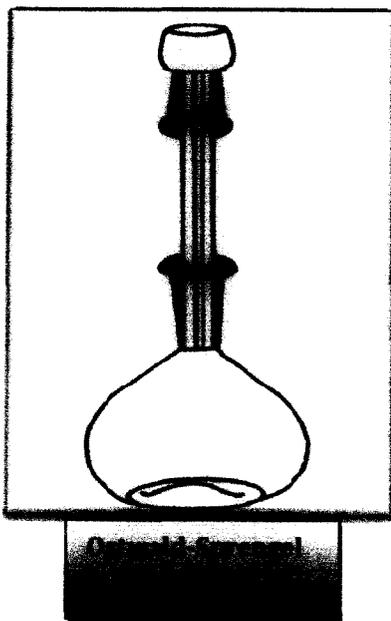


## CHAPTER-III

### **B. EXPERIMENTAL TECHNIQUES**

#### **III.B.1. Measurement of Density:**

Densities ( $\rho$ ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm<sup>3</sup> 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 [29,30]. The



pycnometer filled with air bubble free experimental liquid was kept vertically in a thermostatic water bath maintained at  $\pm 0.01$  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  $\pm 0.01$  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<sup>-3</sup>. 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 [31]. 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 [32-36].

### III.B.2. Measurement of Viscosity:

The kinematics viscosities were measured by means of a suspended-level Ubbelohde [37] 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  $\pm 0.1$ s. The viscometer was always kept in a vertical position in the thermostatic bath with an accuracy of  $\pm 0.01$  K of the desired temperature. The kinematics viscosity ( $\nu$ ) and the absolute viscosity ( $\eta$ ) are given by the following equations.

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

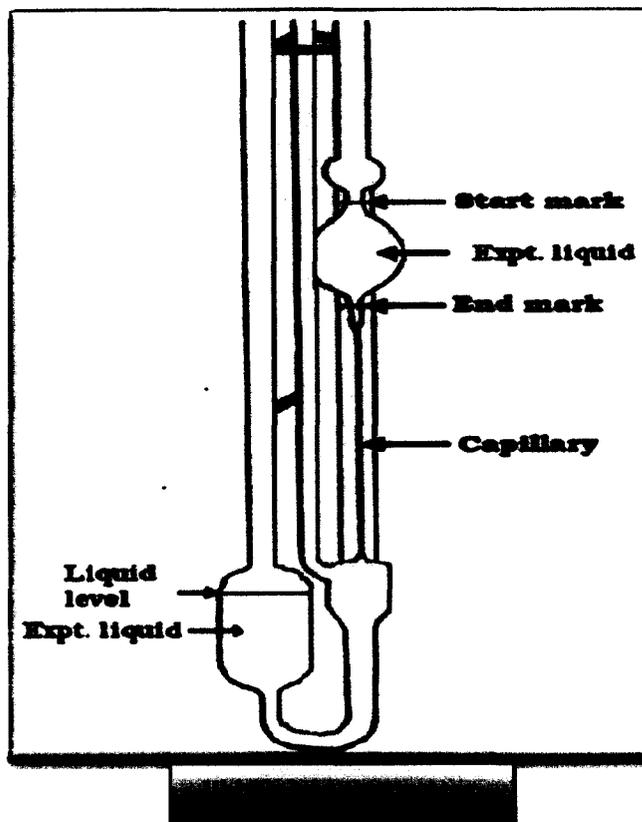
$$\eta = \nu\rho \quad (2)$$

where  $t$  is the average time of flow,  $\rho$  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 calibrating liquids, were found to be  $1.9602 \times 10^{-3}$  and  $4.2019$  respectively. The kinetic energy corrections were done from these values and they were found to be negligible.

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

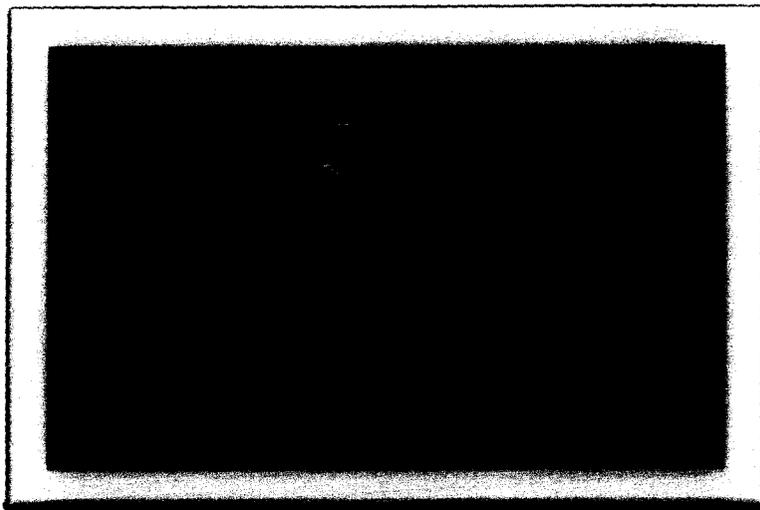
$$\eta_r = \eta/\eta_0 = \rho t/\rho_0 t_0 \quad (3)$$

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 uncertainty in the viscosity measurements, based on our work on several pure liquids, was  $\pm 2 \times 10^{-4}$  mPa.s.



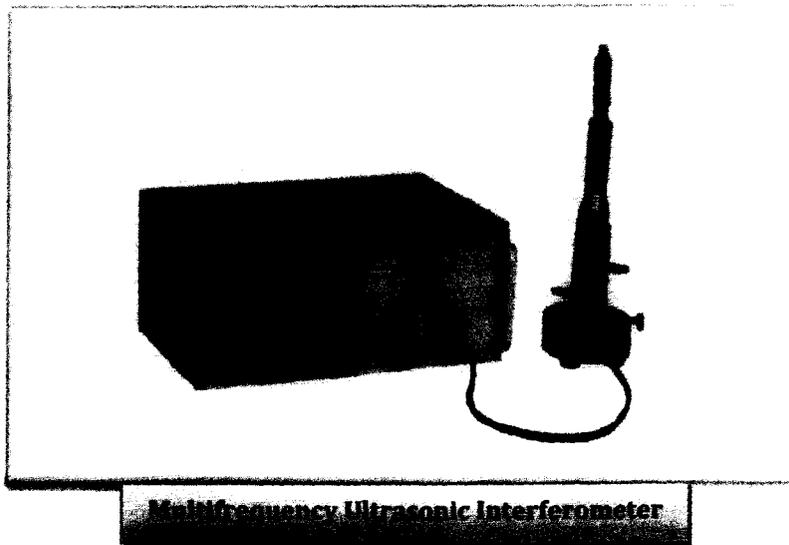
### **Thermostat Water Bath**

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.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<sup>[39]</sup> (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  $\pm 0.01$  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 ( $\lambda$ ) in the medium. Ultrasonic waves of

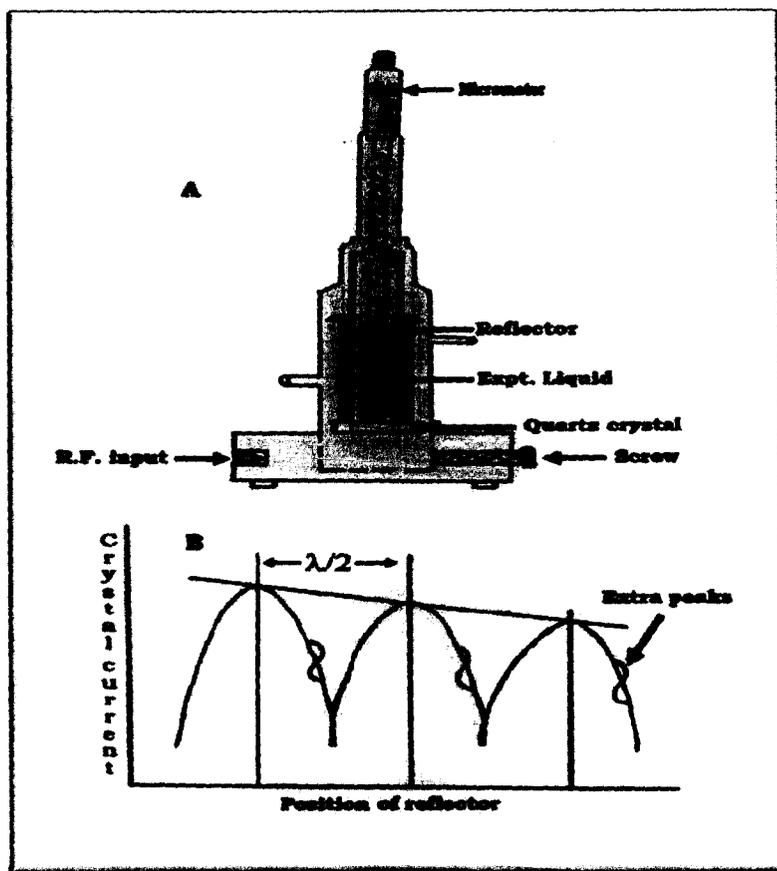
known frequency ( $f$ ) are produced by a quartz crystal fixed at the bottom of the cell.

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 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 ( $\lambda$ ), 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



(B) Cross-section of the measuring cell of a

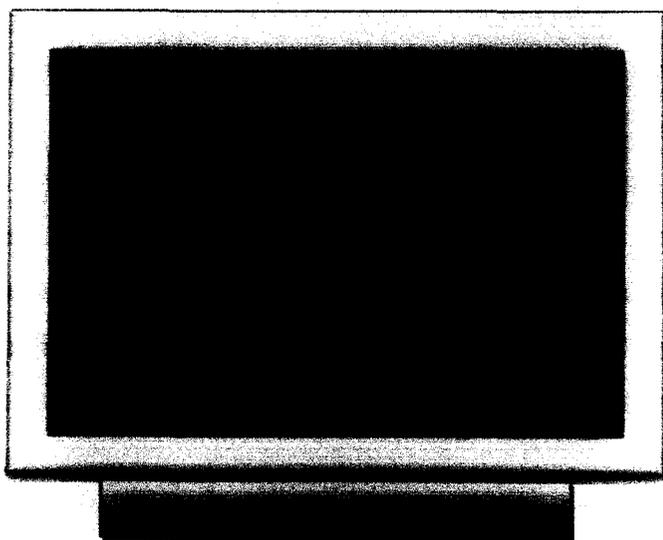
from the quartz crystal till they are reflected back from the movable plate and the standing waves are formed in the liquid in between the reflector plate and the quartz crystal. The micrometer is slowly moved till the anode current on the meter on the high frequency generator deflects a maximum. A number 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 ( $\lambda$ ) 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 ( $\kappa_s$ ) using the following formula:

$$\kappa_s = (u^2 \rho)^{-1} \quad (6)$$

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



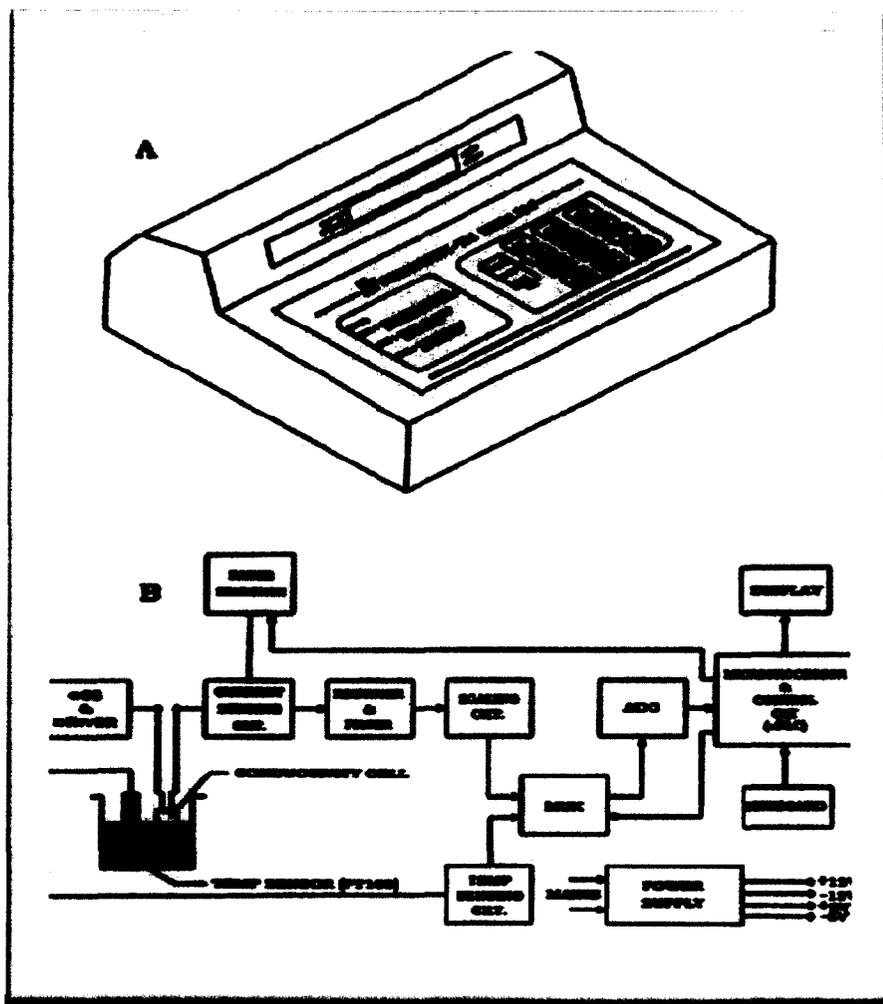
#### III.B.4. Measurement of Conductance:

Systronic Conductivity meter-308 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.

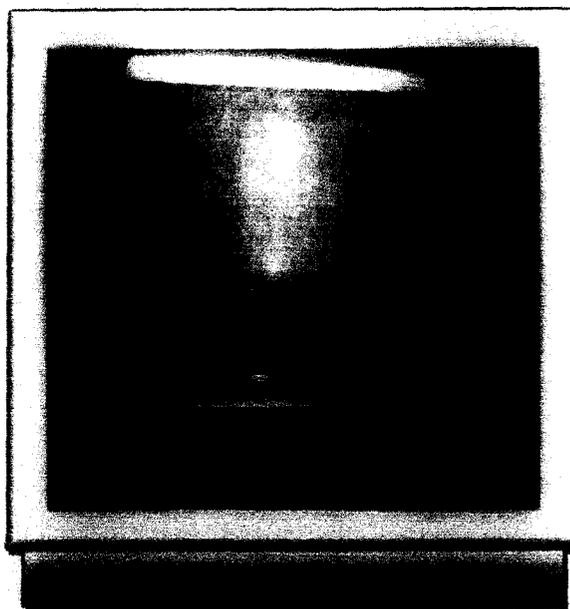
The conductance measurements were carried out on this conductivity bridge using a dip-type immersion conductivity cell, CD-10 with a cell constant of  $1.0 \pm 10\%$   $\text{cm}^{-1}$ . The

instrument was standardized using 0.1 (M) KCl solution. The cell was calibrated by the method of Lind and co-workers<sup>33</sup> The measurements were made in a thermostatic water bath maintained at the required temperature with an accuracy of  $\pm 0.01$  K.



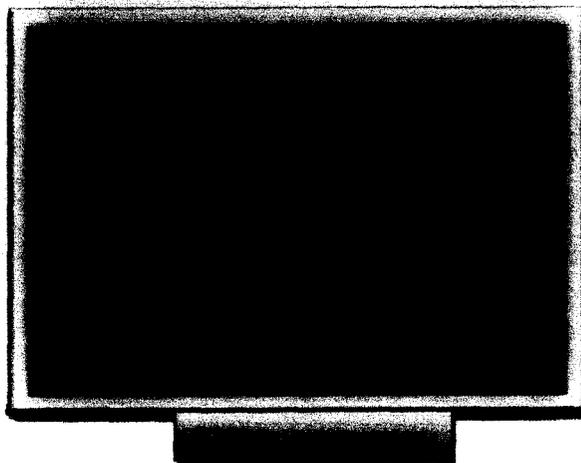
The Sytron's Conductivity meter 308. (A) Isometric

Several solutions were prepared by mass accurate to  $\pm 0.01$  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.



### III.B.5. Measurement of 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 4000-400  $\text{cm}^{-1}$  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 were properly normalized in order to take into account the effective number of absorbers.

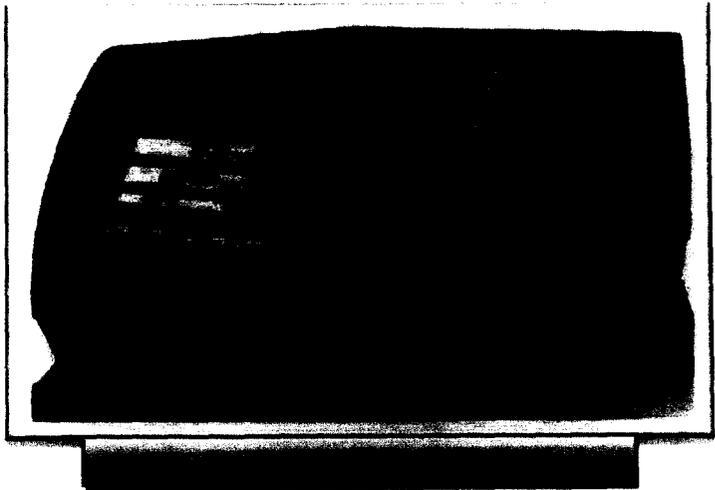
### III.B.6. Measurement of Density:

Densities ( $\rho$ ) were also measured with Digital density meter Anton Paar (DMA 4500 M) GmbH, Austria-Europe.

In the digital density meter, the mechanic oscillation of the U-tube is e.g., electromagnetically transformed into an alternating voltage of the same frequency. The period  $\tau$  can be measured with high resolution and stands in simple relation to the density  $\rho$  of the sample in the oscillator:

$$\rho = A \cdot \tau^2 - B$$

A and B are the respective instrument constants of each oscillator. Their values are determined by calibrating with two substances of the precisely known densities  $\rho_1$  and  $\rho_2$ . Modern instruments calculate and store the constants A and B after the two calibration measurements, which are mostly performed with air and water. They employ suitable measures to compensate various parasitic influences on the measuring result, e.g. the influence of the sample's viscosity and the non-linearity caused by the measuring instrument's finite mass.



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