CHAPTER 2

EXPERIMENTAL

2.1 Viscosity Measurements:

Because of the importance of viscosity in science and technology, numerous instruments known as viscometers for measuring it have been developed to suit different needs. There are two types of methods used to determine viscosity.

i) Capillary Flow Method[1-6]

This is a very satisfactory method for determining viscosity of liquids. This method involves the measure--ment of the volume rate of flow of the fluid through a long cylindrical tube of circular cross section. The total volume 'V' which flows past any cross section in time 't' is

$$V = \frac{\pi P r^4 t}{8 \eta l} \qquad - - - (2.1)$$

This is known as Hagen-Poiseuille equation. Where 'P' is the driving pressure between any two points in a capillary, 'l' is the length of the capillary, η is the coefficient of viscosity, 'r' is the radius of capillary.

ii) Falling Ball Method[1,5,8]

The falling ball method consists of a cylindrical tube filled with the fluid of unknown viscosity. A ball of suitable density and radius is allowed to fall along the axis of the tube. The time at which the ball passes regularly spaced horizontal calibration marks are recorded and is further related to the viscosity of the fluid through suitable mathematical equations.

In the present study, the capillary flow methods was employed to determine the viscosity of fluids at various temperatures. The usual form of this simple, yet accurate apparatus for comparing viscosities of different liquids is shown in figure 2.1. The left hand limbe of the 'U' tube is essentially a pipette with two defining marks 'A' and 'B', and a capillary resistance 'C' through which the liquid contained in bulb 'D' flows under gravity back into the 'E' in the right hand limb. A definite volume of liquid is employed, and is delivered into tube 'F' from a calibrated pipette, the quantity should be such that when the liquid is sucked up into the left hand limb untill the meniscus stands above the mark 'A', then the meniscus on the right stands at the bottom of bulb 'E'. This liquid is released from this position and allowed to flow back. When the meniscus passes mark 'A', a stop

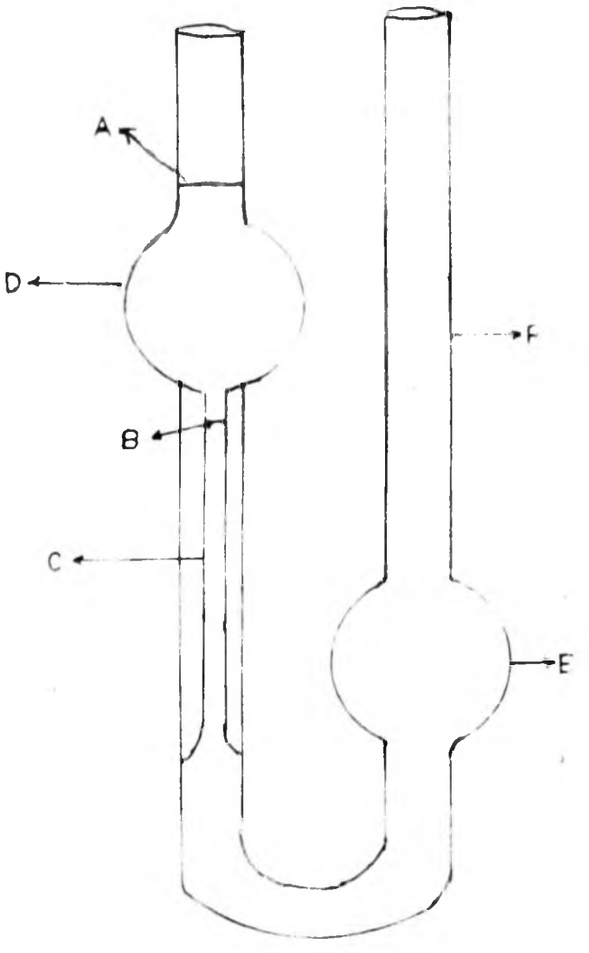

Fig. 2·1 – Viscometer

watch is started and when it reaches mark 'B' the watch is stopped, and the time of out flow is noted. The volume flown from 'A' to 'B' in time 't' is given by equation (2.1). The determination of the absolute viscosity of a liquid with the help of equation 2.1 thus involves the accurate measurement of 'P', 't', 'r', and 'l'. It is usually sufficient to compare the viscosity of the liquid with that of water or other standard liquid by measruing the time taken for equal volumes of the two liquids to flow through the same capillary under press--ures due to their own weights. The densities of both the liquids must be known. The absolute viscosity of the liquid can then be obtained knowing the viscosity of the standard liquid.

The force driving the liquid through the capillary in Ostwald viscometer is equal to $hx\ \rho xg$ where 'h' is the mean difference of level of liquid in the two limbs of the tube, ρ, is the density of the liquid and 'g' the gravitational constant. The resistance to flow depends on the dimensions of the capillary which are constant and on the viscosity of the liquid. If now, the same volume of a second liquid of known visscosity is introduced into the tube, the mean difference of level of the two liquid surfaces will also be h, so that the

driving force is now $h \times \rho_2 \times g$. Thus, the driving force is proportional to the densities of the liquids while the resistance is proportional to their viscosities. Since the rate of flow is proportional to force/resistance, the times of out flow (t_1 and t_2) for the same volume of the two liquids are in the inverse ratio i.e.

$$\frac{t_1}{t_2} = \frac{\eta_1/\rho_1}{\eta_2/\rho_2} \quad \text{or} \quad \frac{\eta_1}{\eta_2} = \frac{\rho_1 \times t_1}{\rho_2 \times t_2} \qquad \text{- - - (2.2)}$$

Thus if the absolute viscosity of one liquid is known, that of the given liquid can be determined.

Since the rate of flow through a capillary tube depends on r^4, and r (the internal radius) can be varied from say 0.2 to 2 mm, Ostwald viscometer can be made to cover a range of 10^4 in viscosity.

2.2 Practical Details:

A viscometer was selected having a flow time of 100 - 300 seconds. It was first throughly cleaned with warm chromic acid so that there were no obstructions in the capillary and the liquid ran clearly without leaving

drops behind. It was then throughly washed by drawing distilled water through it followed by distilled acetone and finally was dried by aspirating clean hot air through it. Compressed air was not used because foreign particles or traces of oil might cause serious errors. The visco--meter was fastned, accurately vertical in a glass sided thermostat as shown in figure 2.2. The mark 'A' was well below the surface. A piece of rubber tubing, cleaned internally to remove dust, was attached to the tube 'A' and used when sucking the liquid into the left hand limb. The temperature of the thermostat was controlled within 0.01 ^{o}C. A mechanical stirrer was used to maintain a uniform temperature of the thermostat. A suitable quan--tity of the liquid under investigation, usually 10 c.c. measured exactly was introduced into the viscometer with a pipette and allowed 10-15 minutes to reach the tempera--ture of the thermostat. The liquids was then sucked up and released, and the time of out flow between the marks was determined with a stop watch reading to 0.01 second. The determination was repeated a number of times (usually 5-6 times). The different readings did not deviate from the mean by more than 0.2 second. To determine the influence of temperature on viscosity, the time of out flow was measured at the interval of 5 ^{o}C between 25 and 40 ^{o}C.

A small error may arise in these measurements due to the change of volume of the liquid owing to expansion but this may be neglected provided that during the out flow period, the lower meniscus lies inside the bulb 'E' so that the change of level is small.

For the purpose of calculating absolute viscosity, densities of the liquids at various temperatures were required. These were determined by means of a pycnometer.

The viscometer was calibrated seperately at each temperature with exactly the same volume of a liquid of known viscosity and density, usually water, the viscosity of which was taken as 0.8007 cp. at 30 ^{o}C.

From the densities and times of flow, absolute vis--cosities of the solvent mixtures and electrolyte solutions were calculated with the help of equation (2.2)

2.3 Density Measurements:

The density of a liquid or solution is defined as the mass per unit volume and is generally expressed as gcm^{-3} in C.G.S. units or more appropriately as kgm^{-3} in SI units. Densities of liquids are generally measured either by weighing a definite volume of the liquid in a density bottle or pycnometer or by determining buoyancy

acting on a 'sinker' immersed in a liquid (principle of Archemedes). Small changes of density are sometimes determined by measuring the rate of rise or fall of a small immersed quartz float of pre-arranged overall density. Where sufficient liquid is available, the density can be determined, approximately, by means of hydrometers.

For the present study pycnometer was used for the density determination, hence a brief survey of various pycnometers is given.

When only small quantities of liquid are available, or where greater accuracy is required, the density of liquid is best determined by means of vessels of accurately defined volume, called pycnometers. These are made in very varying shapes. The pycnometer invented by Spengel and modified by Ostwald is very popular for accurate density measurements.

Perking, Bonsfield and many others altered forms of pycnometers. Most of the pycnometers are of single capillary and usually used to determine the density of a liquid at fixed temperature.

A bicapillary pycnometer (Fig.2.3) having a volume of 15-16 c.c. was chosen for the present work. This allowed an accuracy of about 5 units in the 5th place

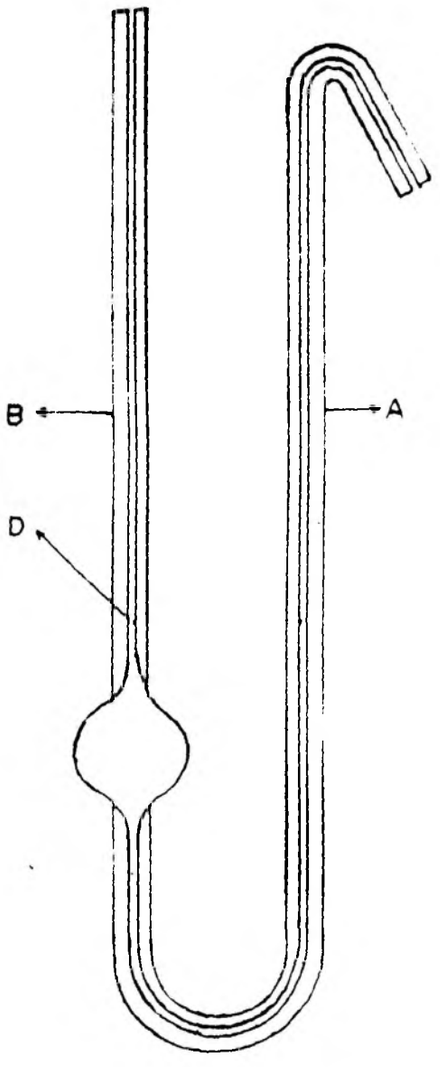

Fig. 2·3– Bicapillary pycknometer

of decimals, which was quite sufficient for our purposes. The pycnometer was washed throughly with chromic acid to remove obstructions in the capillary. This enabled a smooth flow of liquid without drops sticking behind. This was further followed by washing it with distilled water and acetone and then dried with a stream of warm air from hot blower. It was further weighed accurately on Adair Dutt balance having a sensitivity of 0.1 mg. The pycnometer was filled with air free triply distilled water by dipping the end of 'A' limb with the water taken in a beaker. Water filled upto mark 'D' in limb 'B' by capillary action. The pycnometer was weighed again to obtain the mass of water taken in pycnometer. The pycnometer was mounted accurately vertical in a glass sided thermostat. The temperature of the thermostat was controlled within 0.01 ^{o}C. The height of water in limbs 'A' and 'B' say h_1 and h_2 were noted at various tempera--tures and the weight of the water taken in pycnometer, corresponding volumes of water were calculated.

These volumes were plotted against the total height $(h_1 + h_2)$ of water levels yielding a straight line. This served as a calibrating curve for pycnometer.

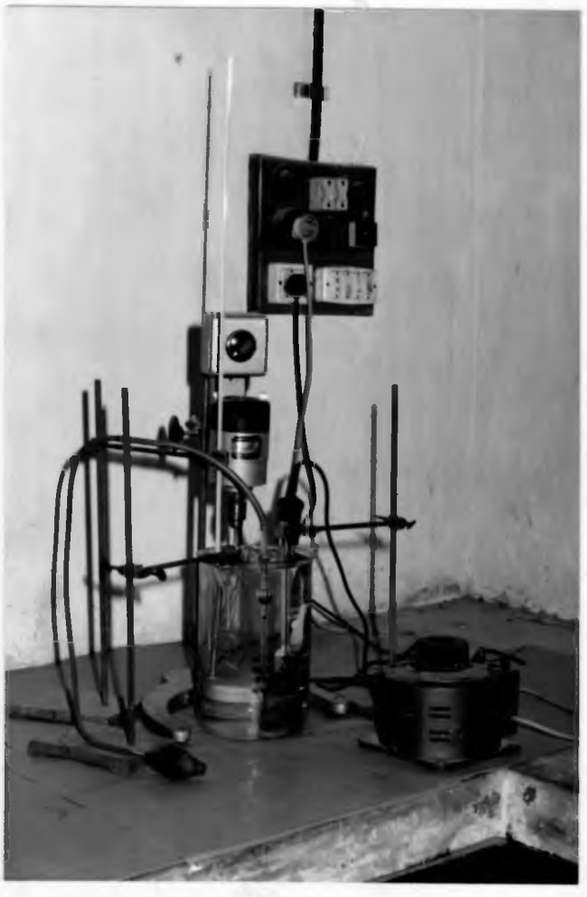

Fig – 2.2

Pycnometer was removed from the thermostat and cleaned as above. It was filled with experimental liquids and mounted in the thermostat. The procedure was repeated to find the total heights (h_1+h_2) for experimental liquids at various temperatures. From these total heights the corresponding volumes of liquids under investigation were obtained from the calibration curve and the corresponding densities determined.

2.4 Ultrasonic Velocity Measurements:

An Ultrasonic interferometer is a simple and direct device to determine the ultrasonic velocity (U) in liquids with a high degree of accuracy.

The principle used in the measurement of 'U' is based on the accurate determination of the wavelength in a 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 wave length, standing waves are formed in the medium. This acoustic resonance gives rise to an electric reaction on the generator driving

quartz crystal and the anode current of the generator becomes maximum.

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

$$\text{Velocity} = \text{Wave length} \times \text{frequency}$$

$$U = \lambda \times f \qquad \text{- - - (2.3)}$$

2.5 Present Work:

In present investigation M-82 Ultrasonic interfero--meter operating at four frequencies was used. The accuracy in velocity measurements was $\pm$ 0.03%. The interferometer was supplied by Mittal enterprises, New Delhi.

This ultrasonic interferometer figure (2.4) consists of the following parts.

A) High frequency generator,

B) Measuring Cell.

A) The High frequency Generator:

This (Fig.2.4) is designed to excite the quartz crystal fixed at the bottom of the measuring cell at its resonant frequency to generate ultrasonic waves in the experimental liquid filled in the measuring cell. A micrometer to observe the changes in current and two controlls for the purpose of sensitivity regulation and initial adjustment of the micrometer are provided on the panel of the high frequency generator.

B) The Measuring Cell:

The measuring cell (Fig.2.4) 'B' is a specially designed double walled cell for maintaining the tempera--ture of the liquid constant during the experiment. A fine micrometer screw has been provided at the top which can raise or lower the reflector plate in the liquid in the cell through a known distance. It has quartz crystal fixed at its bottom. The maximum capacity of the cell is 12 cc.

Adjustment of Ultrasonic Interferometer:

The instrument was adjusted in the following manner.

1) The cell was inserted in the square base socket and

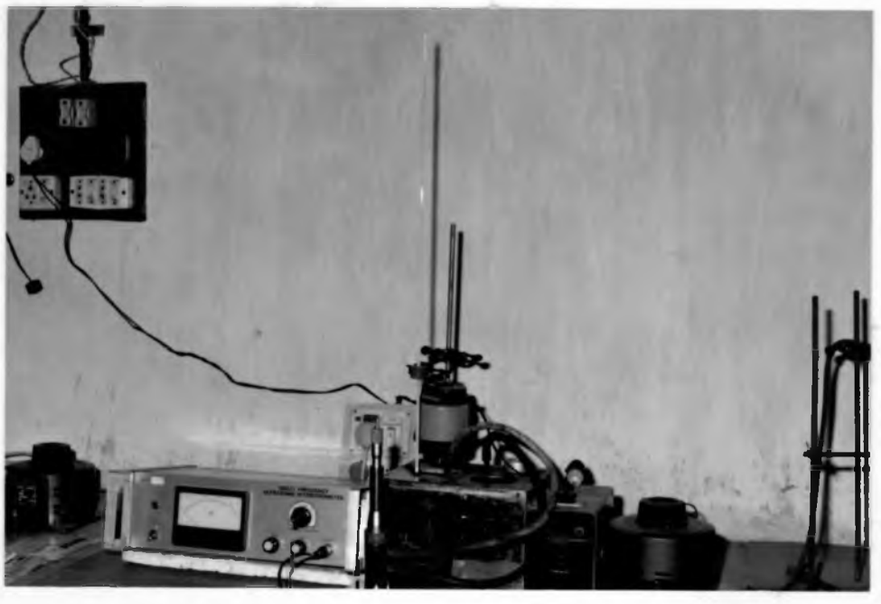

Fig – 2.4

clamped to it with the help of a screw provided on one of its sides.

2) The knurled cap of the cell was unscrewed and lifted away from the double walled cell. Experimental liquid was poured in the middle portion of the cell and the knurled cap was screwed.

3) Water at a desired temperature from a thermostat was circulated through two chutes in double wall of the cell.

4) The high frequency generator was connected to the cell by a co-axial cable.

The interferometer was initially adjusted with the help of two knobs provided on the high frequency generator, one marked with Adj and the other with Gain, with knob marked Adj. The position of the needle on the ammeter was adjusted and knob marked gain was used to increase the sensitivity of the instrument for greater deflection if desired. The meter was used to notice the number of maximum deflections while micro--meter was moved up and down. A number of maxima reading of anode current were taken and their number (n) was counted. The total distance (d) moved by the micrometer thus gave the value of wave length (λ) with the help of following equation.

$$d = n \times \frac{\lambda}{2} \qquad \text{- - - (2.4)}$$

Once the wave length (λ) was known the velocity 'U' in the liquid was calculated with the help of equation (2.3).

2.6 Precautions Taken:

1. The generator was always switched on after filling experimental liquid in the cell.
2. After the experiment, the experimental liquid was taken out and the cell was kept clean and dried.
3. The micrometer was kept open at 25 mm after use.
4. Sudden rise or fall in temperature of circulated liquids was avoided to prevent thermal shock to the quartz crystal.
5. While cleaning the cell, care was taken not to spoil or scratch the gold plating on the quartz crystal.
6. Usually 15 seconds time was given for warming of the generator.

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