CHAPTER 4

TECHNIQUES OF MEASUREMENTS.

4.1 TECHNIQUES FOR MEASUREMENT OF ULTRASONIC VELOCITY:

(a) Optical method:

In this method of measuring sound velocity in liquids, the successive compression and rarefactions of sound waves alter the refractive index of the medium and phase grating is formed [Debye and Sears (1932), Lucas and Biquard (1932)]. If a beam of light is passed through liquid, at right angle to the ultrasonic beam, then the diffraction of light by the sinusoidal phase grating can be used for determination of ultrasonic velocity. Bachem, et al (1934), developed a technique to measure ultrasonic velocity in liquid by directly photographing the compressional waves set up by the ultrasonic beam. Swarup et al (1988) used Debye Sears effect to measure ultrasonic velocity in solution of phenolic and silicon resins in xylene.

(b) Pulse method:

Pellam and Gait (1946), Pinkerton (1949) and Carstensen (1953, 1954) used pulse method for measurement of ultrasonic velocity in solids and liquids. In this method, time required for a pulse to travel forth and back, in the space between source and reflector is measured. The electronic time on an oscilloscope can be used for the time measurement. The precision of this method is a few parts per thousand.

(c) Other modified pulse techniques:

Several pulse techniques with high degree of precision have been developed for ultrasonic studies. Cedrone and Curran (1954), Garnsey et al (1969) and D'arrigo et al (1970) obtained better accuracy by the use of sing around technique Carstensen (1954) and Badar (1968), introduced the differential phase comparison technique for measurement of ultrasonic velocity with an accuracy 0.001%.

Berchmans et al (1983) developed digital ultrasonic velocity meter based on pulse echo technique.

The reverberation method applied at low frequencies (50 Hz to 100 Hz) was developed by Satyabala (1985) for measurement of ultrasonic velocity.

Naik et al (1986) has developed acousto-optic technique for measurement of velocity. Ultrasonic A-Scan opthalmoscope for diagnosis of eye abnormalities is developed by Bindal et al (1986).

A low cost pulsed technique is developed by Agnihotri et al (1987) for measurement ultrasonic velocity in gases and liquids. Following are two draw backs of pulsed techniques.

(i) Large quantity of liquid under investigation is required.

(ii) This techniques requires sophisticated electronic circuitry.

(d) Interferometer method:

Pierce (1925) introduced this technique of measurement of velocity. This technique was then improved by Hubberd and Loomis (1928) and it is based on the formation of standing waves in liquid between the source and the reflector. The movement of the reflector by half wavelength allows the determination of wavelength (\(\lambda\)) of ultrasonic waves in liquid under study. The velocity is calculated as \(U=\lambda f\) where 'U' is the ultrasonic velocity and \(f\) is the frequency of ultrasonic wave. The detection of the positions of the reflector at which the formation of standing waves occur, is usually made by means of the current in high frequency circuit of the source. When the reflector is moved the reaction of the fluid column between source and reflector changes periodically and this can produce periodic variations of the impedance of the source and correspondingly that of the electric current in the high frequency circuit.
Fox (1937) and Hertzfeld (1938) used this method for velocity measurement. Richardson (1940) has developed an interferometer in which the position of the reflector is not changed and hot wire detector is used to measure the amplitude of vibrations of the standing waves. Rao (1970) recommended Lead Zirconate-titanate (PZT) crystal in place of quartz crystal, to take the advantage of piezo-electric properties, such as large frequency band width, low impedance and high electro-acoustical conversion efficiency. Rao et al (1971) employed the double crystal interferometer technique for determining temperature coefficient of ultrasonic velocity in liquids. Sharma et al (1987) and Dewan et al (1988) also used interferometer to study ultrasonic properties of liquids.

(e) Other techniques for velocity measurement:


Interferometer has two advantages over other method (i) It is very simple technique (ii) It requires a small amount of about 10-12 ml of liquid. The effect of reflection of ultrasonic waves from the walls of the cell can be minimised by corrugating the inner wall surface. With these improvement the accuracies better than 0.05%, comparable with the accuracy claimed by pulse method can be obtained by this technique.

In view of the above merits of interferometer technique of ultrasonic velocity measurements, this technique has been used in our laboratory for the study of ultrasonic velocities in polymer solutions. The interferometer supplied by Mittal Enterprises New Delhi was used.
4.2 DESCRIPTION OF THE INTERFEROMETER:

It consists of two parts. (i) High frequency generator, (ii) Measuring cell. The high frequency generator is designed to excite the gold plated quartz crystal to its resonance frequency. It is used to generate ultrasonic waves in the experimental liquid, filled in the measuring cell. A microammeter is provided on the panel of the high frequency generator to observe the changes in the current and two controls are fixed for the purpose of sensitivity regulation and initial adjustment of microammeter.

The measuring cell is double walled cell through which water at constant temperature from a constant temperature water bath can be circulated for maintaining the temperature of the liquid constant during the experiment. A fine micrometer screw is provided at the top, which can lower or raise the reflector plate parallel to itself in the liquid in the cell through known distance. Quartz crystal is fixed at the bottom of the cell. The outer diameter of the cell is 3.96 cm and inner diameter is 1.50 cm and height is 9.25 cm. Its capacity to hold liquid is 12 ml. The least count of micrometer is 0.0001 cm.

The velocity measurements have been done at frequency 2 MHz, 5 MHz, 6MHz, and 7MHz at temperatures 298K, 303K, 308K, 313K and 318K, for each system under study. We have used two such ultrasonic interferometers. One is at a constant frequency of 2MHz. (Model No. F-81). The other is multifrequency interferometer (Model No.F-82) capable of providing ultrasonic waves of frequency 5Mhz, 6Mhz, 7MHz, and 8MHz. The interferometer used is shown in fig. 4.3. The internal details of the cell are shown in diagram of fig. 4.1. The accuracy in the measurement of ultrasonic velocity was ±0.035%. The temperature was kept constant to an accuracy of 0.1 K. by using constant temperature bath with water circulation arrangement. The rubber tubes employed for water circulation were kept of minimum length suiting the arrangement and further these tubes were covered by cotton wrapping to minimise the radiation loss.
4.3 TECHNIQUES FOR THE VISCOSITY AND DENSITY MEASUREMENTS.

In the present work, measurements of viscosity were done using Ostwald viscometer and the measurements of density were done using density bottle. The Ostwald viscometer was kept immersed in constant temperature bath to attain the required constant temperature during measurement of viscosity. The density bottle with liquid sample was also kept immersed in water bath with neck of bottle above the level of water in the water bath, for allowing the over flow through stopper opening. The density bottle was then taken out when overflow ceased and then the stopper opening was closed with an alpin to avoid evaporation of liquid sample. Weights were taken with the help of monopan balance (Model no. K15) supplied by K-Roy and company Varanasi. The sensitivity of the balance is 0.01 mg on the scale range of 100 mg.

4.4 TECHNIQUES FOR MEASUREMENT OF DIELECTRIC CONSTANT.


Digital LCR Q-meter [Model No. 4910] supplied by Aplab has been used in the present work to measure capacitance at 1KHz, from which dielectric constant has been evaluated. The accuracy of this meter is 0.025%.
4.5 SAMPLE PREPARATION:

(i) Tetrahydrofuran obtained from Qualigen fine chemical (A R Grade) was used as solvent. Polymers were obtained from following industries.

(a) PS and PVC from Poly Chemical Industries, Mumbai.

(b) PMMA form Dental Products of India Mumbai.

(c) PIB from Wilson laboratories, Mumbai.

(ii) For each polymer, nine solutions of different weight fractions were prepared separately in fixed volume of THF.

(iii) One solution of PVC and one solution of other polymer were mixed together to give solution mixture for study. The relative concentrations of two polymers were so changed that total weight fraction of two polymers together remains constant and approximately in the range of about 0.0112. (This range was taken for required accuracy of measurement and for the solubility of a substance under a given solvent [Weissberger, 1949]). Nine such sample mixtures were prepared for each system. PVC was the common polymer for each system.

4.6 EXPERIMENTAL MEASUREMENTS OF ULTRASONIC VELOCITY, VISCOSITY AND DIELECTRIC CONSTANT:

(a) Ultrasonic velocity measurements:

A measuring cell filled with polymer solution was mounted in the socket and it was connected to the high frequency generator by coaxial cable. The current in the microammeter was adjusted to maximum. The suitable adjustment was done for maximum gain and zero adjustment setting. Accuracy of adjustment was indicated by sharpness and regularities of peak of the micrometer readings. The micrometer screw was very gradually moved as the reflector travelled through nodal positions till the anode current on the meter shows maximum.

On exciting the crystal, ultrasonic waves travelling through liquid were reflected back from the reflector. So standing waves were formed between crystal and the
reflector. The micrometer screw was slowly moved until the anode current on the meter of generator shows maximum. By knowing total numbers of maxima and total distance 'd' travelled by micrometer, wavelength \( \lambda \) can be calculated as follows

\[
d = n \left( \frac{\lambda}{2} \right)
\]

The velocities of ultrasonic waves at frequencies 2, 5, 6 and 7 MHz were calculated using formula

\[
c = \lambda f
\]

(b) **Viscosity measurements**:

Viscosity measurements were made with Ostwald viscometer. The viscosity of polymer solution is given by relation.

\[
\eta_1 = \eta_2 \left( \frac{\rho_1 t_1}{\rho_2 t_2} \right)
\]

Where

- \( \eta_1 \) = Viscosity of polymer liquid mixture.
- \( \eta_2 \) = Viscosity of water.
- \( \rho_1 \) = Density of polymer liquid mixture.
- \( \rho_2 \) = Density of water.
- \( t_1 \) = Time required for level of polymer solution to fall between the two marks on viscometer.
- \( t_2 \) = Time required for level of water to fall between two marks on viscometer.

(c) **Dielectric constant measurements**: (i) Cylindrical condenser:

The cylindrical condenser, used for measurement of capacitance of liquids, was fabricated in the laboratory. The condenser consists of two coaxial brass cylinders having outer diameter 3.5 cm and inner diameter 2 cm. The height of cylinders was 4 cm. They are fixed coaxially being separated by glass spacers. The condenser was kept immersed completely in the liquid of definite volume contained in a glass beaker. This makes the experimental liquid to be contained in the space between the two coaxial cylinders with same area of liquid in contact with the
two electrodes.

(ii) Determination of correction factor for glass spacers:

In cylindrical condenser, glass rods are used as spacers. This condenser with air and glass spacers constitutes a parallel combination of two condensers of capacities $C_a$ for air and $C_g$ for glass spacers with resultant capacity $(C_a + C_g)$. This condenser of resultant capacity $(C_a + C_g)$ is kept in a glass beaker and is connected in unknown arm of the LCR bridge (Q meter). The Q-meter is digital and autocompute. It gives the capacity of parallel combination and it is denoted by $C_1$. The liquid solution of known dielectric constant is added to the beaker, untill the cylindrical portion is completely submerged in liquid. This forms a parallel combination of $C_{L}$ (liquid) and $C_g$. Again LCR Q-meter computes the resultant capacity of this combination. It is denoted by $C_2$. If $\varepsilon$ is the dielectric constant of liquid solution then

$$C_a + C_g = C_1$$

$$C_g + C_{L} = C_2$$

$$\varepsilon = \left\{ \frac{C_{L}}{C_a} \right\} = \left\{ \frac{(C_2 - C_g)}{(C_1 - C_g)} \right\}$$

By knowing, $C_1$, $C_2$ & $\varepsilon$, value of $C_g$, the correction factor is determined. In this way the value of $C_g$ is determined by using four pure solvents of known dielectric constant. During the measurement of capacity, following precautions are taken. The leads connecting the terminals of the condenser to the LCR Q-meter are kept as short as possible. Connecting wires used are shielded cables and that the position of the leads is kept fixed and same throughout the measurements. This helps in avoiding stray capacitance and that the lead capacitance remains constant, which gets eliminated due to difference in capacity measurements. The system consisting of cylindrical condenser and glass beaker are further kept in a metallic, double walled chamber, between the walls of which water is circulated at constant temperature from constant temperature waterbath.
(iii) Dielectric constants of experimental polymer solutions:

The cylindrical condenser was kept immersed completely in solution of sample polymers of which dielectric constant is to be determined. The digital auto compute Q-meter gives the capacity of the condenser with solution. On knowing capacitance with air as dielectric and correction factor $C_g$, the dielectric constant of polymer solution is calculated using formula,

$$\varepsilon = \frac{C_2 - C_g}{C_1 - C_g}$$

4.7 LIST OF SAMPLE PAIRS (IN THF) STUDIED IN THE PRESENT WORK:

(1) System I Polyvinyl chloride (PVC) + Polystyrene (PS).
(2) System II Polyvinyl chloride (PVC) + Polymethyl methacrylate (PMMA).
(3) System III Polyvinyl chloride (PVC) + Polyvinyl acetate (PVAc).
(4) System IV Polyvinyl chloride (PVC) + Polyisobutylene (PIB).
FIG. 4-1

LINE DIAGRAM SHOWING INNER DETAILS OF ULTRASONIC INTERFEROMETER
FIG 4.2 CYLINDRICAL CONDENSER PLACED INSIDE DOUBLE WALLED CHAMBER
Ultrasonic Interferometer

To measure ultrasonic velocities in liquids
Table 4.1
Experimental and literature values of sound velocity for finding error of measurements.

Temp. = 25°C (298K)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Liquid</th>
<th>Experimental value</th>
<th>Literature value</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzene</td>
<td>1295.4 m/s</td>
<td>1295 m/s*</td>
<td>0.032</td>
</tr>
<tr>
<td>2</td>
<td>Carbon disulphide</td>
<td>1148.6 m/s</td>
<td>1149 m/s*</td>
<td>0.040</td>
</tr>
<tr>
<td>3</td>
<td>Acetone</td>
<td>1169.6 m/s</td>
<td>1170 m/s*</td>
<td>0.033</td>
</tr>
<tr>
<td>4</td>
<td>Carbon tetrachloride</td>
<td>0930.3 m/s</td>
<td>0930 m/s*</td>
<td>0.030</td>
</tr>
</tbody>
</table>

Table 4.2
Experimental and literature values of dielectric constants for finding error of measurements.

Temp. = 25°C (298K)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Liquid</th>
<th>Experimental value</th>
<th>Literature value</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzene</td>
<td>2.3733</td>
<td>2.373</td>
<td>0.0120</td>
</tr>
<tr>
<td>2</td>
<td>Toluene</td>
<td>2.378</td>
<td>2.38</td>
<td>0.08</td>
</tr>
<tr>
<td>3</td>
<td>Carbon disulphide</td>
<td>2.585</td>
<td>2.586</td>
<td>0.038</td>
</tr>
<tr>
<td>4</td>
<td>Carbon tetrachloride</td>
<td>2.231</td>
<td>2.230</td>
<td>0.044</td>
</tr>
</tbody>
</table>

Table 4.3
Mean correction factor Cg for glass-spacers. (298K)

Temp. = 25°C (298K)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Medium</th>
<th>Capacitance 298K</th>
<th>Literature 298K</th>
<th>ε</th>
<th>Cg</th>
<th>Mean Cg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Air</td>
<td>6.9PF</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Cyclohexane</td>
<td>11.604PF</td>
<td>2.22</td>
<td>3.044</td>
<td>3.041</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>O-Cresol</td>
<td>47.43PF</td>
<td>11.50</td>
<td>3.020</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>M-Cresol</td>
<td>48.59PF</td>
<td>11.80</td>
<td>3.039</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Hexane</td>
<td>10.278PF</td>
<td>1.876</td>
<td>3.043</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

References * Physical and Chemical constants by T.H. Laby and G.W.C. Kaye, 12th Edn., 1958, P-61
### Table 4.4
Ultrasonic Velocity (U) in THF (at 2 MHz)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Temp. in K</th>
<th>Temp. in °C</th>
<th>U Experimental</th>
<th>U Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>298 K</td>
<td>25 °C</td>
<td>127000 cm/s</td>
<td>126300 cm/s@ (at 3MHz)</td>
</tr>
<tr>
<td>2</td>
<td>303 K</td>
<td>30 °C</td>
<td>125000 cm/s</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>308 K</td>
<td>35 °C</td>
<td>124000 cm/s</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>313 K</td>
<td>40 °C</td>
<td>121500 cm/s</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>318 K</td>
<td>45 °C</td>
<td>119000 cm/s</td>
<td></td>
</tr>
</tbody>
</table>

### Table 4.5
Dielectric Constants of THF.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Dielectric Constant ( \varepsilon ) (Experimental)</th>
<th>Temp.</th>
<th>Dielectric Constant ( \varepsilon ) (Literature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.94</td>
<td>30 °C</td>
<td>7.0 ( (25^\circ \text{C}) )#</td>
</tr>
<tr>
<td>2</td>
<td>6.90</td>
<td>35 °C</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>6.86</td>
<td>40 °C</td>
<td></td>
</tr>
</tbody>
</table>

### Table 4.6
Dielectric Constant \( \varepsilon \) at (1 MHz)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Polymer (Solid)</th>
<th>Literature value ( \varepsilon ) at 293K</th>
<th>Literature value ( \varepsilon ) at 298K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Polyvinyl chloride (PVC)</td>
<td>4.00*</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Polystyrene (PS)</td>
<td>2.55*</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Polymethyl methacrylate (PMMA)</td>
<td>2.60*</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Polyvinyl acetate (PVAc)</td>
<td>4.00*</td>
<td>2.7**</td>
</tr>
<tr>
<td>5</td>
<td>Polyisobutylene (PIB)</td>
<td>2.21*</td>
<td></td>
</tr>
</tbody>
</table>

References
- Physical Chemistry of Polymer by A Tager, (1972) P-281, Mir Publisher Moscow.
Table 4.7
Experimental and Literature Values Of $\rho$, $\eta$, $U$, $\beta$, $\tau$ And $\alpha/f^2$ For THF:

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Parameter</th>
<th>Temp.</th>
<th>Expt. value</th>
<th>Lit. value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Density ($\rho$)</td>
<td>303K</td>
<td>0.8813 gm/cm$^3$</td>
<td>0.8815 gm/cm$^3$*</td>
</tr>
<tr>
<td>2</td>
<td>Viscosity ($\eta$)</td>
<td>303K</td>
<td>0.52X10$^{-2}$ Poise.</td>
<td>0.4335X10$^{-2}$ Poise **</td>
</tr>
<tr>
<td></td>
<td></td>
<td>298K</td>
<td>0.55X10$^{-2}$ Poise ***</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Ultrasonic velocity ($U$)</td>
<td>303K</td>
<td>125000 cm/sec. (at 2MHz).</td>
<td>126420 cm/sec. (at 3MHz).</td>
</tr>
<tr>
<td>4</td>
<td>Adiabatic compressibility ($\beta$)</td>
<td>303K</td>
<td>7.262X10$^{-11}$ cm$^2$/dyne.</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Relaxation Time ($\tau$)</td>
<td>303K</td>
<td>0.5035X10$^{-12}$ sec (at 2MHz).</td>
<td>0.4063X10$^{-12}$ sec ** (at 3MHz).</td>
</tr>
<tr>
<td>6</td>
<td>Classical absorption coefficient($\alpha/f^2$)</td>
<td>303K</td>
<td>0.7942X10$^{-16}$ sec$^2$/cm (2MHz)</td>
<td>0.6343X10$^{-16}$ sec$^2$/cm** (at 3MHz).</td>
</tr>
</tbody>
</table>

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