CHAPTER 2

MATERIALS AND

EXPERIMENTAL METHODS
2.1 METHODS OF PURIFICATION OF CHEMICALS

All the chemicals used are of AnalaR grade. Commercially obtained chemicals were further purified wherever necessary.

Dimethylsulphoxide (BDH)

Dimethylsulphoxide was dried over freshly ignited quick lime and then vacuum distilled. The middle fraction was collected and vacuum distilled. The process was repeated until the electrical conductivity of the sample was $10^{-7} \ \Omega^{-1} \text{cm}^{-1}$. The purified sample was degassed by successive cycles of cooling and pumping, and then stored over mercury out of contact with air in the dark. It was found that bubble formation occurred on mixing unless the component was carefully degassed.

Water

Deionised water (Permutet process) was distilled thrice. To each litre of distillate was added 0.5 g of sodium hydroxide and 0.2 g of potassium permanganate. This alkaline solution was slowly distilled from an all Pyrex glass vessel and the middle fraction was collected. The purity of the sample was checked by measuring the conductivity ($1 \times 10^{-6} \ \Omega^{-1}\text{cm}^{-1}$).

Dimethylformamide

N,N-Dimethylformamide (E.Merck) sample was purified and used. The commercial material is allowed to stand over solid KOH for several hours and then fractionated at 5 mm pressure. The specific conductance of dimethylformamide obtained is $0.8-1.2 \times 10^{-6} \ \Omega^{-1} \text{cm}^{-1}$. 
Mercury

Mercury was first run in a fine stream through a long length of 5 per cent nitric acid and the process was repeated a second time and the sample was finally passed through a column of water. It was then dried by means of filter paper and run through a hardened filter paper with a pin hole at the apex of the cone. The dried sample was finally distilled thrice under reduced pressure using Gallen Kemp mercury distillation apparatus.

Polymers

The specifications of the polymers used are given in the Table 2.1

<table>
<thead>
<tr>
<th>Name</th>
<th>Grade</th>
<th>Molecular weight</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(acrylic acid)(PAA)</td>
<td>AnalR</td>
<td>2000</td>
<td>Aldrich Chemicals Co., Inc., USA</td>
</tr>
<tr>
<td>Poly(methacrylic acid)(PMAA)</td>
<td>AnalR</td>
<td>30000</td>
<td>Wilson Laboratories, Mumbai, India</td>
</tr>
<tr>
<td>Poly(vinyl acetate)(PVAc)</td>
<td>AnalR</td>
<td>25000</td>
<td>Wilson Laboratories, Mumbai, India</td>
</tr>
<tr>
<td>Poly(ethylene oxide)(PEO)</td>
<td>AnalR</td>
<td>300000</td>
<td>BDH, UK</td>
</tr>
<tr>
<td>Poly(vinyl pyrrolidine)(PVP)</td>
<td>AnalR</td>
<td>40000</td>
<td>SISCO Laboratories, Mumbai, India</td>
</tr>
<tr>
<td>N,N-Dimethylformamide (DMF)</td>
<td>AnalR</td>
<td>73.10</td>
<td>E.Merck, India</td>
</tr>
<tr>
<td>Dimethylsulphoxide (DMSO)</td>
<td>AnalR</td>
<td>78.13</td>
<td>Qualigens, India</td>
</tr>
</tbody>
</table>
2.2 PREPARATION OF POLYMER BLEND SOLUTIONS

The blends of various polymers with varying compositions were prepared by solution blending technique. Solutions of both polymers were prepared in solvents (i.e., dimethylsulphoxide or dimethylformamide) separately at room temperature and shaken well to dissolve polymer thoroughly. The required proportions of each polymer solution was mixed either by mechanical means or occasional shaking. The solution was allowed to stand undisturbed for 24 hrs to observe any phase separation. This ensures complete phase equilibrium state. If phase separation had not occurred after 24 hrs, the polymer blend solution was used for measurements. If the mixture indicated phase separation then it was diluted using the respective solvents till it remained as a single phase for 24 hr. The solution thus prepared was used for the studies.
2.3 DENSITY MEASUREMENTS

Density is determined by two methods in the present study. (a) Pycnometer method, (b) Specific gravity bottle method.

(a) Pycnometer Method

This method is used to determine the density of dilute polymer blend solutions. Pycnometers of different designs have been used for accurate measurements by several workers. In the present investigations, pycnometer of Parker and Parker type with minor modifications has been employed. The double stem pycnometer with a bulb of capacity 25 ml on one of the stems was used in the studies as shown in the Fig. 2.1. The stems are made of pyrex glass tube of bore of about 3 mm and bent to the sides making an obtuse angle at the bend. The vertical part of the stem containing the bulb is of 5 cm length and carries a mark in the middle to read the liquid level. A mark is also made on the second stem at about the same level to read the difference between the liquid levels in the two stems. The inclined part of each stem is 4 cm. The enlargement of the stem serves as over flow cup where liquids are raised to temperatures above the room temperature. The open ends of the stems are closed by suitable teflon caps in order to prevent the loss of liquid due to evaporation.

The following procedure is adopted for filling the pycnometer and weighing.

Procedure

The well cleaned and dried pycnometer is weighed accurately with reference to another pycnometer of the same design, weight and surface area is hung to the hook of the pan containing the weights. The liquid is introduced
Fig. 2.1. Pycnometer
into the weighed pycnometer with the help of a syringe without air bubbles, approximately up to the marks on the stems. The pycnometer is kept immersed vertically in a thermostatic bath maintained at the desired temperature with the ends of the stems closed with the caps for about half-an-hour. This permits the unfilled part of the stem to be drained completely and allows liquid-vapour equilibrium to be established. The amount of the liquid at initial filling is adjusted to allow for expansion (or contraction) due to the difference in temperature between the bath and surroundings. The distance between the mark and the liquid meniscus in both the stems is determined with the aid of a travelling microscope which reads with a precision of 0.002 cm. The pycnometer is then removed from the hook and weighed after about 15 minutes. The reference pycnometer hung from the hook of the other pan is also subjected to the same treatment to eliminate the errors in weight due to moisture condensation on the surface of the pycnometer.

The volume of the pycnometer is calculated from the weight of the water filling the pycnometer up to the marks exactly. The weight of water at the required temperature filling the volume of pycnometer included between the marks is determined as described below.

The capillary used to prepare the stems is filled with mercury and the length of the mercury thread is measured with the help of the travelling microscope. The internal radius (r) of the capillary is calculated from the length of the mercury column. The uniformity of the bore of the tube is also checked by a similar procedure. The volume (dV) of water enclosed between the mark and the liquid meniscus is calculated by using the formula \( \pi r^2 h \) (where \( r \) is the radius of capillary, \( h \) is the distance between the mark and the meniscus). The difference between the volume of water actually present in the pycnometer
and the volume of water that fills exactly up to the mark at the required temperature gives the volume \( dV \) of water enclosed between the mark and the liquid meniscus. The weight \( dW \) of water equal to this volume \( dV \), is calculated by multiplying \( dV \) with the density of water at that particular temperature (taken from literature). The mass \( w \) of water filling the pycnometer up to the marks is obtained by subtracting or adding \( dW \), as the case may be from or to the weight of water actually filling the pycnometer at the required temperature. The experiment is repeated till reproducible results with an accuracy of one in \( 10^4 \) parts is obtained. By dividing this weight \( W \) by the density of water at that particular temperature the exact volume of the pycnometer can be calculated.

In the determination of the density of any liquid first the pycnometer is filled with the liquid such that the liquid meniscus is as close as possible to the mark on the pycnometer.

The pycnometer with the liquid is kept immersed in the thermostat at the required temperature for sufficient time such that the level of the liquid is constant in both the limbs. The height of the liquid level above or below the reference mark as the case may be is measured with the travelling microscope. The weight "\( W \)" of the liquid in the pycnometer is determined by the procedure similar to that described earlier.

The exact volumes and masses of test liquids introduced into the pycnometer were determined in a similar way and their densities were computed from the equation, \( \rho = \frac{M}{V} \, \text{g/cm}^3 \). The measured values of density are accurate to \( \pm 0.01\% \).
b. Specific Gravity Bottle method

This method is employed to determine the density of viscous polymer blend solutions. The density of polymer blend solution ($\rho$) of different proportions and the pure solvents ($\rho_0$) have been measured by this method. The volume of the specific gravity bottle has been standardized using double distilled water at 30, 35, 40 and 45°C. The density is given by the relation

$$\text{Density} = \frac{\text{Weight of liquid mixture}}{\text{Weight of water}} \times \text{Density of water at that temperature}$$

The densities of water at above mentioned temperatures have been taken from the literature\(^1\). In order to maintain the temperature constant, the specific gravity bottle with the experimental liquids is immersed up to the neck in the thermostat with a thermal stability of $\pm 0.05^\circ C$. The accuracy in the measurement of density employing specific gravity bottle is better than $\pm 0.01\%$. Weight measurements in the present study are made by employing a electric balance capable of measuring up to 0.0001 g.
2.4 VISCOSITY MEASUREMENTS

The coefficient of viscosity or dynamic viscosity \( \eta \) is defined as the force per unit area necessary to maintain a unit velocity gradient between two parallel planes which are at a unit distance apart.

Viscosities of liquids, liquid mixtures and polymer solutions can be determined either by absolute method or by relative method. Excellent review of these methods are available in literature\(^1\). The determination of viscosity by absolute method\(^2,3\) requires the determination of the constants of the apparatus. This involves a laborious procedure. Hence, viscosities of liquids, liquid mixtures and polymer solutions were determined by the relative method, in that there is no need to determine such constants for the apparatus. It is easy to measure the viscosity of a liquid by comparison with a reference standard liquid of known viscosity. Different types of viscometers and their modifications and conditions of viscosity measurements have been described by McGoury and Mark.\(^4\) In the present study, viscosities of liquids and polymer solutions were determined by relative method using Ubbelohde viscometer\(^5,6\) (Fig. 2.2). This is superior over the Ostwald type of Cannon Fenske Viscometers as it is not required to fill with definite volume of liquid and not required to make corrections for temperature to the viscometer constant. In the Ubbelohde viscometer\(^7\) the liquid is induced to flow only down the walls of the bulb below the capillary, thus forming a suspended level in the form of a hallow hemisphere at the lower end of the capillary to discharge into an airspace. This eliminates the uncertainty regarding the position of the lower liquid level and balance the effect of surface tension at the upper meniscus.

The viscometer is fabricated with a heavy walled glass so that the instrument is resistant to shock. The bulb between etched lines (Ubbelohde bulb) has a capacity of about 4 ml and the capillary tube had a length of about
FIGURE 2.2. Ubbelohde viscometer
90 mm and 0.5 mm of internal diameter. The reservoir of the viscometer was filled with the sample liquid by tilting the viscometer about 30° from the vertical and its limbs closed with teflon caps. The viscometer was kept for about 30 minutes in a thermostat maintained at required temperature with ± 0.05°C. This permits the contents of the viscometer to attain experimental temperature. Then the teflon caps were removed and the sample was raised to the middle of the upper most bulb by applying suction, with the air vent being closed by the finger tip. The efflux time was measured between the marks on either side of the bulb with a stop watch which had an accuracy of ± 0.1 Sec. The efflux time of each sample was measured at least eight times. The average efflux time and density at the same temperature were employed in the calculation of viscosity. The viscosities (η) of pure liquids and polymer solutions were computed from the efflux time and densities using the relation

$$\eta = K_v \cdot \frac{d}{t} \quad \ldots \quad 2.1$$

where 'K_v' is viscometer constant, 'd' and 't' are density and efflux time for a given sample respectively. At the experimental temperature 'K_v' was evaluated using viscosity and density of pure water at 30°C from the relation

$$K_v = \frac{\eta_w}{d_w \times t_w} \quad \ldots \quad 2.2$$

The calibration of viscometer was checked by measuring the viscosities of pure liquids like benzene, cyclohexane and carbon tetrachloride at 30°C. The measured values of viscosity are accurate to ± 0.1%.
2.5 ULTRASONIC VELOCITY MEASUREMENTS

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

Principle

The principle used in the measurement of velocity (v) is based on the accurate determination of the wavelength (λ) in the medium. Ultrasonic waves of known frequency (f) (2 MHz in the present study) are produced by a quartz plate fixed at the bottom of the cell. The waves are reflected by a movable metallic plate (reflector) kept parallel to the quartz plate. If the separation between these two plates is exactly equal to the multiples of the sound wavelength, standing waves are formed in the medium. The acoustic resonance gives rise to an electrical reaction on the generator driving the quartz plate and the anode current of the generator becomes maximum.

If the distance is now increased or decreased with the help of the micrometer screw, and the variation is exactly one half wavelength (λ/2) or multiple of it, anode current again becomes maximum. From the knowledge of wavelength (λ), the velocity (v) can be calculated by the relation

\[
v = \lambda f \]

In the present investigation, a single crystal variable path interferometer was used to measure the ultrasonic velocities.

Description

The ultrasonic interferometer consists of the following parts.

a. The High Frequency Generator
b. The Measuring Cell
a. The High Frequency Generator

It is designed to excite the quartz plate 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 controls 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

This is a specially designed double walled cell for maintaining the temperature of the liquid constant during the experiment. A fine micrometer screw has been provided at the top which can lower or raise the reflector plate in the cell through a known distance. It has quartz plate fixed at its bottom.

A sketch of the interferometer cell is shown in Fig. 2.3. The interferometer cell is made of stainless steel, which is in the form of tube of inner diameter 1.6 cm with capacity 12 cm$^3$. A gold plated quartz plate of diameter 0.9 cm is cemented at the bottom of the interferometer cell. The ultrasonic waves start from the quartz plate and they are reflected back from the movable reflector. The reflector used in this interferometer is a fused quartz rod with a reflecting surface of 1.4 cm in diameter. This is coupled to a micrometer screw assembly reading up to 0.01 cm using a teflon coupler via the steel rod. The micrometer screw activates the steel rod which is spring loaded to take care of any back lash. The micrometer assembly along with the reflector is fixed to the liquid cell with the help of a threaded cup and teflon ring. The required stability for the measuring cell is given by a heavy pedestal, provision has been made for circulating water at any desired temperature from a thermostatically controlled bath into a jacket around the measuring space to
Fig. 2.3. Interferometer cell.
maintain the experimental liquid at a constant temperature during the experiment.

A crystal controlled r.f. oscillator (Fig. 2.4) is used to excite the transducer at a fixed frequency of 2 MHz. The HT current to the output tube is fed through a bridge network including a micrometer in such a way that the changes in the plate current can be easily observed on the micro-ammeter. Two controls are provided for the purpose of sensitivity regulation and initial current adjustment of the meter. The interferometer consists of an electrically dried quartz plate coupled to the liquid column. The length of the liquid column can be varied by moving the quartz reflector, keeping its plane parallel to the quartz plate. Whenever the distance between the transducer and the reflector corresponds to an integral number of half-wavelengths, the liquid column vibrates in resonance resulting in an increase of the motional impedance of the transducer. This leads to a sharp dip in the r.f. voltage across the transducer. The current vibrations are noted in the microammeter. The distance covered by the reflector between any two consecutive dips corresponds to one-half wavelength, $\lambda / 2$.

**Measurement of Velocity**

The measuring cell filled with the experimental liquid and was connected to the output terminal of the high frequency generator through a shielded cable. When the generator is switched on, the ultrasonic waves move normal from the quartz plate 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 plate.

Water was circulated at required temperature around the measuring cell from a thermostat. When the liquid attained the temperature of the bath,
the micrometer screw was slowly moved till the anode current meter showed a maximum and the reading of the micrometer was recorded. A number of maximum readings of anode current are passed and their number 'n' is counted. The distance between the quartz transducer and the reflector plate was displaced by moving the screw. To increase the measuring accuracy several maxima were passed and their number 'n' was counted. The anode current was finally adjusted at the maximum and the reading of the micrometer was again noted. The total distance 'd' moved by the micrometer (reflector) was calculated by using the following relation

\[ d = n \lambda / 2 \]  \hspace{1cm} (2.4)

where \( \lambda \) can be calculated. Once the wavelength (\( \lambda \)) is known, the frequency of the crystal 'f' being accurately known (2 MHz), the sound velocity 'v' in the liquid can be calculated with the help of the following relation

\[ v = f \lambda \]  \hspace{1cm} (2.5)

Finally the velocities were corrected for diffraction affects, and the values are accurate to 1 to 1000 meters. The velocities of some pure liquids measured using the interferometer are found to agree with the literature values.
2.6 REFRACTIVE INDEX MEASUREMENTS

Refractive index (nD) measurements of the polymer blend solutions of different proportions and the pure solvents have been made at different temperatures employing the abbe refractometer (M/s Mittal Enterprises, New Delhi). The construction of this instrument is illustrated in Fig. 2.5.

The Abbe refractometer essentially consist of two glass prisms A and B. The hypotenuse surface of prism B is polished while that of A is finely ground. The two prisms are enclosed in metal castings hinged at H. The two prisms can be rotated about a horizontal axis immediately beneath a telescope T and they can be held in contact with the help of a clamp C. An arm R which is attached with the metal case carrying the prisms moves along a graduated scale, the reading of which gives directly the refractive index of the liquid under examination.

In order to maintain the temperature constant, the prisms A and B are enclosed in a water jacket J. Thermostated water from a thermostat with a thermal stability of ± 0.05°C is circulated through this jacket. The graduated scale is calibrated using double distilled water as the reference. The values of refractive index of water are taken from the literature. Sodium vapour lamp (λ = 5893 Å) is used as the source of light.

The refractive index is directly read by moving the index arm of the refractometer until the field seen through the eye piece is one half dark. The compensator (Amie prisms) drum is adjusted to remove all colour from the field. The index arm is then adjusted by means of the vernier until the dividing line between the light and dark portions of the field exactly coincide with the intersection of the cross wires as seen in the eye piece. In order to make the dividing line sharp, a tracing paper is placed over the reflecting mirror. This
Fig. 2.5. Abbe refractometer
provides a better source of diffused light. The prisms are cleaned with soft tissue moistened with the solvent first and then with acetone. The accuracy of the refractive index measurement is ± 0.2%.
REFERENCES


