Experimental
This chapter deals with the specifications of the chemicals used and the methods of their purification. It also includes the description of the experimental techniques viz. excess molar volume, ultrasonic speed, viscosity, FT-IR and FT-NMR.

3.1. Chemicals and their sources

The chemicals used in the present work are listed in table 1 along with their sources and grades.

Table 1: Sources and grades of chemicals.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Sources</th>
<th>Grades</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-Ethanediol</td>
<td>Fluka AG (Buchs)</td>
<td>purum &gt; 99.5 (GC)</td>
</tr>
<tr>
<td>1,3-Propanediol</td>
<td>Fluka AG (Buchs)</td>
<td>purum &gt; 99.0% (GC)</td>
</tr>
<tr>
<td>1,2-Butanediol</td>
<td>Fluka AG (Buchs)</td>
<td>purum &gt; 99.0% (GC)</td>
</tr>
<tr>
<td>1,3-Butanediol</td>
<td>Merck (India)</td>
<td>HPLC &gt; 99.0% (GC)</td>
</tr>
<tr>
<td>1,4-Butanediol</td>
<td>Merck (India)</td>
<td>HPLC &gt; 99.0% (GC)</td>
</tr>
<tr>
<td>2,3-Butanediol</td>
<td>Merck (India)</td>
<td>HPLC &gt; 98.0% (GC)</td>
</tr>
<tr>
<td>1,5-Pentanediol</td>
<td>Fluka AG (Buchs)</td>
<td>purum &gt; 96.0% (GC)</td>
</tr>
<tr>
<td>Pyrrolidin-2-one</td>
<td>Fluka AG (Buchs)</td>
<td>purum &gt; 99.0% (GC)</td>
</tr>
<tr>
<td>N,N-Dimethylformamide</td>
<td>Fluka AG (Buchs)</td>
<td>purum &gt; 99.9% (GLC)</td>
</tr>
<tr>
<td>β-Cyclodextrin</td>
<td>Fluka AG (Buchs)</td>
<td>purum &gt; 99.0% (HPLC)</td>
</tr>
</tbody>
</table>

3.2. Purification of the chemicals

1,2-Ethanediol was dried with sodium hydroxide and distilled under vacuum.

1,3-Propanediol and 1,3-butanediol were dried with anhydrous sodium sulphate and fractionally distilled.

1,2-Butanediol was fractionally distilled under reduced pressure then fractionally crystallized by partial freezing.

2,3-Butanediol was first treated by repeated fractionally recrystallization. Next it was fractionally distilled under reduced pressure.
1,4-Butanediol and 1,5-pentanediol were fractionally distilled in an 18-in. Stedman column and then distilled in vacuo over sodium hydroxide pellets.

Pyrrolidin-2-one was dried with calcium oxide and fractionally distilled.

\( N,N\)-Dimethylformamide was dried over magnesium sulphate for 24 hours and then over potassium hydroxide. It was distilled at atmospheric pressure and the middle fraction was retained.

\( \beta \)-Cyclodextrin was dried under vacuum at temperature between 333.15 and 343.15 K for several days before use.

Mercury required for the experiments was purified by washing it several times with 5% nitric acid followed by distilled water till it was free from acid. After drying, it was double distilled under reduced pressure.

The distilled chemicals were stored over the molecular sieves type A4 in sealed dark bottles before use. The purity of chemicals was checked by measuring densities with the help of an Austrian precision densimeter Anton Paar (Model DMA 60). The measured density values for all the components are listed in table 2. A close agreement is observed with literature values. Table 2 also enlists the values of various physical constants of the pure components.

### 3.3. Excess molar volume measurements

#### 3.3.1. Dilatometer construction

A continuous dilution dilatometer of the type described by Dickinson et al. [173] has been used for the measurement of excess molar volumes of the binary mixtures. The outline of the dilatometer is illustrated in figure 55. The mixing bulb 'A' containing one liquid component is connected by means of a narrow bore capillary to the glass tube 'B' which is calibrated with mercury before making it a part of dilatometer. The volume change is measured by the movement of the mercury level in calibrated capillary 'D' which is connected via \( B_{sp} \) quickfit joint at 'E' to the dilatometer. Stopcock 'F' is provided for adjustment of the initial mercury level h in the capillary 'D'. The cathetometer readings are taken when the stopcock is closed. A small magnetic bead is put in the mixing bulb 'A' before sealing it. This is used for stirring the mixture rotating a magnet over it.
Table 2: Molar masses $M$, boiling points $T_b$, melting points $T_m$, experimental densities $\rho_{\text{exp}}$, literature densities $\rho_\text{lit}$, critical temperatures $T_c$, critical pressures $P_c$, critical volumes $V_c$, refractive indices $n_D$, vapour pressures $P$, ultrasonic velocities $u$, isobaric thermal expansivities $\alpha_p$, and molar isobaric heat capacities $C_p$ for the liquid components at 308.15 K.

<table>
<thead>
<tr>
<th>Component</th>
<th>$M$ /g mol$^{-1}$</th>
<th>$T_b$ /K</th>
<th>$T_m$ /K</th>
<th>$\rho_{\text{exp}}$ /kg m$^{-3}$</th>
<th>$\rho_\text{lit}$ /kg m$^{-3}$</th>
<th>$T_c$ /K</th>
<th>$P_c$ /MPa</th>
<th>$V_c$ /m$^{-3}$mol$^{-1}$</th>
<th>$n_D$</th>
<th>$P$ /MPa</th>
<th>$u$ /m s$^{-1}$</th>
<th>$\alpha_p$ /$10^5$ K$^{-1}$</th>
<th>$C_p$ /J K$^{-1}$mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-Ethanediol</td>
<td>62.07</td>
<td>470.45</td>
<td>260.55</td>
<td>1102.90</td>
<td>1102.50$^c$</td>
<td>630.95</td>
<td>75.95</td>
<td>47.60</td>
<td>1.4310$^e$</td>
<td>0.012$^f$</td>
<td>1633.36</td>
<td>6.770$^i$</td>
<td>149.7$^i$</td>
</tr>
<tr>
<td>1,3-Propanediol</td>
<td>76.10</td>
<td>487.60</td>
<td>246.45</td>
<td>1042.70</td>
<td>1043.71$^b$</td>
<td>639.90</td>
<td>59.49</td>
<td>61.42</td>
<td>1.4386$^e$</td>
<td>1.300$^f$</td>
<td>1604.47</td>
<td>7.002$^i$</td>
<td>176.4$^i$</td>
</tr>
<tr>
<td>1,2-Butanediol</td>
<td>90.12</td>
<td>467.15</td>
<td>159.15</td>
<td>988.25</td>
<td>991.43$^c$</td>
<td>623.77</td>
<td>50.11</td>
<td>72.60</td>
<td>1.4341$^e$</td>
<td>1.300$^f$</td>
<td>1422.61</td>
<td>10.077$^i$</td>
<td>228.8$^i$</td>
</tr>
<tr>
<td>1,3-Butanediol</td>
<td>90.12</td>
<td>480.72</td>
<td>223.15</td>
<td>991.28</td>
<td>994.20$^c$</td>
<td>643.24</td>
<td>50.11</td>
<td>73.30</td>
<td>1.4363$^e$</td>
<td>0.008$^f$</td>
<td>1496.03</td>
<td>9.326$^i$</td>
<td>218.4$^i$</td>
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<tr>
<td>1,4-Butanediol</td>
<td>90.12</td>
<td>501.0</td>
<td>292.89</td>
<td>1003.95</td>
<td>1006.47$^e$</td>
<td>666.69</td>
<td>48.15</td>
<td>73.32</td>
<td>1.4428$^e$</td>
<td>1.330$^f$</td>
<td>1577.76</td>
<td>8.595$^i$</td>
<td>202.1$^i$</td>
</tr>
<tr>
<td>2,3-Butanediol</td>
<td>90.12</td>
<td>455.2</td>
<td>295.65</td>
<td>990.72</td>
<td>990.74$^c$</td>
<td>612.63</td>
<td>51.41</td>
<td>74.83</td>
<td>1.4388$^e$</td>
<td>0.130$^f$</td>
<td>1456.60</td>
<td>8.201$^i$</td>
<td>225.8$^i$</td>
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<tr>
<td>1,5-Pentanediol</td>
<td>104.15</td>
<td>515.6</td>
<td>515.6</td>
<td>974.30</td>
<td>974.30</td>
<td>649.37</td>
<td>41.46</td>
<td>83.46</td>
<td>1.4484$^e$</td>
<td>1.330$^f$</td>
<td>1566.12</td>
<td>11.280$^i$</td>
<td>233.2$^i$</td>
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<tr>
<td>Pyrrolidin-2-one</td>
<td>85.11</td>
<td>518.00</td>
<td>298.00</td>
<td>1097.14</td>
<td>1099.13$^d$</td>
<td>568.55</td>
<td>55.40</td>
<td>62.07</td>
<td>1.4840$^e$</td>
<td>1.300$^f$</td>
<td>1599.97</td>
<td>9.775$^i$</td>
<td>169.4$^i$</td>
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<tr>
<td>N,N-Dimethylformamide</td>
<td>73.09</td>
<td>426.2</td>
<td>212.72</td>
<td>935.55</td>
<td>935.10$^d$</td>
<td>641.87</td>
<td>44.34</td>
<td>49.29</td>
<td>1.4282$^e$</td>
<td>0.490$^f$</td>
<td>1426.03</td>
<td>8.895$^i$</td>
<td>185.0$^i$</td>
</tr>
</tbody>
</table>

$^a$Ref. [68], $^b$Ref. [50], $^c$Ref. [40], $^d$Ref. [82], $^e$Ref. [84], $^f$Ref. [41] and $^i$Ref. [172].

$^c$ and $^b$ represent temperature 298.15 and 303.15 K respectively.

$^{1}$, $^{12}$, $^{14}$, $^{15}$ and $^{i6}$ derived from density [68], [50], [171], [40], [82] and [84] respectively.

Rest is of Ref. 171.
3.3.2. Calibration of the capillaries and the tube

The capillaries are calibrated by measuring the length of mercury thread in each capillary and subsequently weighing it. Appropriate corrections are made for the hemispherical shape of the meniscus on each end of the thread. The ratio of the volume to the corrected length of the thread is used as the calibration factor of the capillary. Only those capillaries are used for which the calibration factor varies only within 0.1 percent over the entire capillary length.

For the calibration of the glass tubing, it is sealed at one end and clamped vertically. Weighed amounts of mercury are added from the open end in small lots and the length of mercury level is measured each time with the help of the cathetometer. The ratio of the volume to the length of mercury is used as the calibration factor of the glass tube. Each tube is calibrated at least twice and the most uniform portion is used in the construction of the dilatometer.

3.3.3. Cleaning of the dilatometer

The dilatometer is rinsed with chromic acid and washed several times with water, alcohol and acetone and finally dried under vacuum. In subsequent experiments, rinsing twice or thrice with acetone and then drying under vacuum is found to be sufficient.

3.3.4. Thermostat and temperature control

Excess molar volume measurement requires a very efficient temperature control in the water thermostat. For better results, temperature control is achieved using a circulating water bath, regulated to ± 0.01 \( K \), using a proportional temperature controller. The temperature is calibrated to 308.15 ± 0.01 \( K \) with a precision platinum resistance thermometer. The absolute temperature is measured using Beckmann thermometer calibrated against a standard thermometer.

3.3.5. Vacuum line

A vacuum line, used for the degassification of pure liquids consists of a mercury diffusion pump, a rotary oil pump, a McLeod gauge and arrangement for connecting the sample holders. The liquid in the degassification cell is first frozen with the help of liquid nitrogen and then the cell is connected to the vacuum line for 2-3 minutes. The stopcock is then closed and the liquid is melted. The procedure is repeated 6-8 times until there is no air bubble in the liquid.
A - Mixing bulb
B - Glass tube
D - Capillary
E - Quickfit joint
F,S - Stop cocks

Figure 55: Continuous Dilution Dilatometer
3.3.6. Working of the dilatometer

In the continuous dilatometer stopcock '5' (figure 55) is cleaned and partly greased (to avoid contact with mercury and liquids) before each filling of the dilatometer. The dilatometer is connected via the $B_w$ quickfit joint at 'E' to the vacuum line. The flask containing pure distilled mercury is connected with the help of a pressure tubing to the stem connecting the dilatometer with the vacuum line. The mercury is allowed to fill the dilatometer under vacuum upto the glass joint 'E'. Care is taken that no air bubble is present within the apparatus at this or at any subsequent stage.

With stopcock 'S' open, degassed component 1 is introduced into the mixing bulb 'A' with the help of a glass syringe with a long flexible needle. The syringe needle is passed through stopcock 'S' by bending before injection of the component. The exact quantity of component 1 in the bulb 'A' is determined from the difference in weight of the glass syringe (with the needle) before and after addition of the component. Stopcock 'S' is then closed. Similarly, the degassed component 2 is injected into the glass tube 'F' with the help of the syringe. The dilatometer is assembled as shown in figure 55. It is clamped in a constant temperature water thermostat with only the top of the glass tube 'G' protruding above the water level. After nearly half an hour when the thermal equilibrium is attained, the cathetometer readings are taken at $h_1$ and $h_2$.

By successive dilution of one liquid component with the second component, it is possible to cover the entire composition range in two experiments by interchanging the components in bulb and the tube respectively. On opening the stopcock 'S', component 2 in bulb 'B' is introduced into the mixing bulb by the hydrostatically induced flow of mercury from 'A' to 'B'. Component 2 is then introduced into the mixing bulb 'A' by carefully operating the stopcock '5'. The mercury level $h_1$ is corrected by estimating the length of mercury thread in the capillary connecting the glass tube with the mixing bulb. Cathetometer readings of $h_1$ and $h_2$ are taken until constancy of level $h_2$ is maintained relative to some fixed mark. Component 2 is added in small amounts by opening stop-cock 'S' and the mixture stirred in the mixing bulb by the movement of the magnetic bead with a strong rotating magnet surrounding the bulb.
Experimental

The number of moles of the component 1 added in the bulb A are calculated from the weight of the component 1 added in the mixing bulb and that of component 2 from the length of the mercury displaced from the glass tube B. The excess molar volume is calculated from the change in the mercury height in the precalibrated capillary D, using equation

$$V^E (cm^3 mol^{-1}) = \frac{C \Delta h}{n_1 + n_2}$$

where C is the volume per cm of the capillary D. \(\Delta h\) is the change in height of mercury and \(n_1\) and \(n_2\) are the number of moles of component 1 and 2 respectively.

After determining the excess molar volume at one set of compositions, the dilatometer is cleaned and filled with double distilled mercury in the same manner as describe above. The degassed component 2 is introduced in the mixing bulb A and component 1 in the tube B. The whole procedure is repeated and excess molar volumes are calculated using equation (1).

3.3.7. Calculation of excess molar volume

Weight of syringe $= a g$

Weight of syringe + solvent $= b g$

Weight of solvent A added $= (a-b) g = W_1 g$

Molecular weight of solvent A $= M_1$

Number of moles of solvent A added, \(n_A\) $= W/M_1$

Initial reading of tube length $= X cm$

Final reading of the tube length after transferring solvent B in the mixing bulb from the glass tube $= Y cm$

Total difference in the tube length $= (X-Y) cm = L cm$

Volume of solvent B added $= C x L cm^3$

Actual volume added $= (C x L - C_j) cm^3 = V cm^3$

Weight of solvent added \(W_2\) $= V x \rho$

Molecular weight of solvent B $= M_2$

Number of moles of component B, \(n_B\) $= W_2/M_2$

Total number of moles $= n_A + n_B$

Mole fraction of solvent A $= n_A/(n_A + n_B)$
Total change in height of mercury level in the capillary = $\Delta h$

and excess molar volume, $V^E/(cm^3 mol^{-1}) = \Delta h C/(n_1 + n_2)$

where $C_1 (= 0.7111801 \, cm^3/cm)$, $C_2 (= 0.0020886 \, cm^3 mol^{-1})$ and $C_3 (= 0.00586 \, cm^3/cm)$ are the calibration factors of the tube, volume correction of the capillary and calibration factor of the extension respectively for the dilatometer used in the present study.

3.3.8. Precision of the method and estimation of errors

The precision of excess molar volume was checked by measuring $V^E$ of standard system, benzene + cyclohexane at 308.15 K. The measured $V^E$ values were found to be good agreement with literature [174].

The final expression to calculate excess molar volume contains a number of measurable quantities. It is important, therefore, to ascertain how the errors in individual measurements affect the results.

If $U = f(X, Y, ...)$ and errors for $U, X, Y, ...$ are $\pm U, \pm X, \pm Y, ...$, then the total error in measuring $U$ is given by equation

$$(\Delta U)^2 = \left(\frac{\partial U}{\partial X}\right)^2 (\Delta X)^2 + \left(\frac{\partial U}{\partial Y}\right)^2 (\Delta Y)^2 \tag{2}$$

In most cases it is found that there are one or two principle sources of error, and all the other measurements incur negligible error.

The excess molar volume $V^E$ is related to experimental quantities by equation

$$(1) \quad V^E/(cm^3 mol^{-1}) = \frac{C\Delta h}{n_1 + n_2}$$

The total uncertainty $V^E$ in excess molar volume can be estimated from the uncertainties in various measured quantities on the right hand side of equation (1) and can be written as

$$(\Delta V^E)^2 = \left(\frac{\partial V^E}{\partial C}\right)^2 (\Delta C)^2 + \left(\frac{\partial V^E}{\partial \Delta h}\right)^2 (\Delta \Delta h)^2 + \left(\frac{\partial V^E}{\partial \Delta n_1}\right)^2 (\Delta \Delta n_1)^2 + \left(\frac{\partial V^E}{\partial \Delta n_2}\right)^2 (\Delta \Delta n_2)^2$$

$$= \left(\frac{h}{n_1 + n_2}\right)^2 (\Delta C)^2 + \left(\frac{C}{n_1 + n_2}\right)^2 (\Delta \Delta h)^2 + \left(\frac{Ch}{(n_1 + n_2)^2}\right)^2 (\Delta \Delta n_1)^2 + \left(\frac{Ch}{(n_1 + n_2)^2}\right)^2 (\Delta \Delta n_2)^2 \tag{3}$$
where $\Delta C$ is the uncertainty in the measurement of capillary diameter, $\Delta h$ the uncertainty in the measurement of the difference in two heights (initial and final levels of mercury), $\Delta n_1$ the uncertainty in the measurement of the weight of component 1 i.e. uncertainty in the difference of weight of syringe before and after the injection of the component 1, $\Delta n_2$ the uncertainty introduced while reading Cathetometer scale for measuring component 2 added before and after the addition and $h = \Delta h$ is the total change in height of mercury level in the capillary.

Taking into account the various uncertainties in the experimentally measured quantities i.e. $\Delta C$, $\Delta h$, $\Delta n_1$ and $\Delta n_2$ which are of the order $2 \times 10^{-5}$, $3 \times 10^{-3}$, $1 \times 10^{-4}$ and $2 \times 10^{-3}$ respectively. The excess molar volume measurements are accurate within $\pm 0.002 \text{ cm}^3\text{mol}^{-1}$.

3.4. Measurements of ultrasonic speed

Ultrasonic speed measurements stand as one of the primary techniques for study of properties of matter such as mechanical, electromagnetic and particle interactions. The propagation of high frequency stress waves is determined by the measurement of velocity and attenuation of ultrasonic waves as a function of any environmental variable such as temperature, pressure etc.

The ultrasonic speed and attenuation in the liquids can be determined by two standard techniques

1. Continuous wave method (CW method)
2. Pulse echo method (PE method)

The CW method is generally adopted in KHz regions. For low loss specimen, it is possible to achieve high sensitivities with this method. The CW method suffers from
- The presence of extra complicating modes of vibrations
- Boundary effects
- The need for larger energy dissipation and subsequent heating of the system.
- Lack of good accuracy and precision.

The pulse echo (PE) method overcomes most of the limitations of the CW method and is widely used. In the commonly used pulse echo technique an ultrasonic frequency burst is introduced into the sample through a piezo-electric transducer.
bonded to the specimen. The ultrasonic pulse travels through the sample and an echo is registered each time it returns to the transducer. The amplitude of successive echoes decrease exponentially due to attenuation in the sample. In general the amplitudes are related by

\[ A_2 = A_1 e^{-\alpha d} \]  

(4)

where \( A_1 \) and \( A_2 \) are amplitudes of echoes, \( d \) and \( x \) are the distance travelled by ultrasonic wave between registering the two echoes and attenuation coefficient respectively.

The above equation yields

\[ x = \frac{1}{d} (\ln A_1 - \ln A_2) \]  

(5)

Ratio of two amplitudes is generally expressed in decibles or nepera.

Thus

\[ x = \frac{2.303}{d} \log_{10} \left( \frac{A_1}{A_2} \right) \text{ db/unit length} \]  

(6)

or

\[ x = \frac{1}{d} \log_{10} \left( \frac{A_1}{A_2} \right) \text{ nepera/unit length} \]  

(7)

For measuring the velocity of the ultrasonic wave, time elapsed between registering \( A_1 \) and \( A_2 \) (\( \tau \)) is to be measured accurately. Then velocity \( (u) \) in the sample is given by

\[ u = \frac{d}{\tau} \]  

(8)

Oscilloscope is the simplest equipment by which one can measure both attenuation and velocity. Obviously, simpler the equipment, cruder will be the measurement. Some of the widely used methods to measure velocity to high resolution and accuracy are

1. Sing around system
2. Pulse-echo-overlap method
3. Pulse superposition technique.
Pulse-echo-overlap (PEO) technique is very powerful technique because it is possible to make absolute as well as relative measurements with high degree of accuracy. As both the echoes, involved in the measurement obtained in PEO method, pass through the same electronic system, any change in transit time of various devices employed will introduce zero error. It is also insensitive to system gain changes including attenuation changes in the sample. The absolute accuracy of velocity measurement using this technique is as high as 2 parts in 10⁴.

The other advantages of PEO method over the other-method are:
1. It may operate either with the transducer bonded directly to specimen or with buffer rod interposed between the transducer and specimen.
2. It may be operated with broadband pulses as well as rf bursts.
3. It can be set up to make through transmission measurement of travel time on single pass between two transducers.

3.4.1. Principle of measurement

The principle of measurements is to make two signals of interest overlap on the oscilloscope by driving the X-axis with a frequency whose period is the travel time between the signals of interest. Then one signal appears on one sweep of the oscilloscope and the other signal appears on the next sweep. The X-axis frequency is supplied by CW oscillator. For jitter-free overlap, the signals of interest must be synchronised with in the phase of the CW voltage. This condition is achieved by generating the repetition rate of the input pulse from the phase of CW voltage by a frequency divider. Division by a large number (e.g. 1000) allows the echoes from one pulse to be attenuated before the next pulse is applied. The output of the frequency divider is a trigger signal, synchronous with the phase of CW voltage. The trigger signal triggers the main pulser, which pulses the transducer. A diode limiter circuit keeps the input pulse from overloading the amplifier. The main pulser also triggers two intensifying pulses, which are applied to Z-axis of the scope, to intensify the trace. This feature is necessary to distinguish the two signals of interest from the rest of the echoes in the trace.

3.4.2. Method of measurement

In the measurements, the oscilloscope is first set on the triggered mode of operation. The delays and widths of intensity pulse are then adjusted to cover the signals of interest. The frequency of CW oscilloscope is set at approximately the
reciprocal of travel time between signals of interest. The oscilloscope is then switched to drive $X$-axis mode of operation. The intensity of cathode ray tube is turned down so that only the intensified peaks are visible, and the main pulser delay is adjusted so that these signals are in the center of the screen. Then CW oscillator frequency is adjusted, so that the two signal overlap as shown in figure 56. In the pulse echo overlap method, an overlap will appear not only when time between signals of interest is equal to reciprocal of CW oscillator frequency but also for any integer multiple ‘$m$’ of CW oscillator. This means that the two echoes will appear on $m^{th}$ and $2m^{th}$ sweeps of oscilloscope instead of on first and second after the occurrence of input pulse. Old echoes can be deleted by noise on base line and in interference with in the echoes. The advantage in going to large multipliers is in minimizing the influence of $+1$ count error in counter, counting CW frequencies. With a large frequency, $\pm 1$ is smaller fractional error. The ultrasonic cell is calibrated by using two or three solvents of high purity and of known ultrasonic velocity value. Initially the values of time ($\tau$) are determined for the solvents and then the value of the distance $d$ is calculated from $\tau$ and known $u$ values.

For the ultrasonic cell used in the present work, the value of $d$ is 0.03187776 m determined using distilled water, acetonitrile, methanol and cyclohexane as the pure solvents. This value of $d$ is further used to calculate the values of ultrasonic velocity of all the system studied for which the similar procedure is followed.

3.4.3. Estimation of error

The ultrasonic velocity of a liquid mixture is related to the experimental quantities by the equation (8)

$$u = \frac{d}{\tau}$$

The total uncertainty ($\Delta u$) in ultrasonic velocity may be written as
Experimental

\[(\Delta u)^2 = (\frac{\partial u}{\partial d})^2 (\Delta d)^2 + (\frac{\partial u}{\partial \tau})^2 (\Delta \tau)^2 \]  

(9)

where \( \Delta d \) is the uncertainty in the measurement of distance traveled by ultrasonic wave between registering the two echoes and \( \Delta \tau \) is uncertainty in measurement of time taken to travel the distance.

Taking into account the various uncertainties in the experimentally measured quantities \( i.e. \) \( d \) and \( \tau \) which are of the order \( 1 \times 10^{-6} \) and \( 1 \times 10^{-4} \) respectively. The ultrasonic velocity measurements are accurate within \( \pm 2 \times 10^{-2} \text{ ms}^{-1} \).

3.5. Measurements of viscosity

Viscosity measurements are made using a modified form of a Ubbelohde viscometer (figure 57) placed in a water thermostat, the temperature of which is controlled to \( 308.15 \pm 0.01 \) K. The basic relation for the capillary viscometry is the Poiseuille’s law:

\[ \eta = \frac{\pi Fr^4 \rho}{8VL} \]  

(10)

where \( \eta \) is the coefficient of viscosity in Poise, \( P \) is driving pressure or constant vertical pressure in dyne cm\(^{-2} \) for maintaining a uniform rate of flow, \( r \) the radius of the capillary in cm, \( V \) the volume of the liquid in cm\(^3 \) which flows through the capillary, \( t \) is time of flow in seconds and \( L \) is the length of the capillary in cm.

Equation (10) holds accurately for streamlined flow but not for turbulent flow, which sets in at high velocity. It does not include kinetic energy correction terms. If the driving pressure is due to force of gravity, then

\[ P = h\rho g \]  

(11)

where \( h \) is the height of the driving head, \( \rho \) is density of the liquid and \( g \) is acceleration due to gravity. The equation then becomes

Figure 57. Modified form of Ubbelohde Viscometer
The exact equation for the laminar flow of a liquid through a cylindrical tube may be written as

$$\eta = \frac{r^4 h_{pgt}}{8VL}$$

(12)

where \( n \) is coefficient associated with flow at the end of the capillary.

More accurately, stream-lined flow through a tube or capillary is expressed by Bingham et al. [175] and Reimen [176] as

$$\eta = \frac{r^4 h_{pgt}}{8V(L + nr)} - \frac{m\rho V}{8\pi(L + nr)t}$$

(13)

where \( m \) is another coefficient associated with flow at the end of the capillary.

The first term incorporates the law determined experimentally by poiseuille and second term arises from the work done in accelerating and decelerating the fluids at the end of the capillary. Martin [177] has used the formula in a simplified form as

$$\eta = A\rho t - \frac{B\rho}{t}$$

(15)

or

$$\frac{\eta}{\rho} = At - \frac{B}{t}$$

(16)

where

$$A = \frac{r^4 h_{pg}}{8V(L + nr)} = \text{constant}$$

(17)

$$B = \frac{mV}{8\pi(L + nr)} = \text{constant}$$

(18)

\( A \) and \( B \) are viscometer constants and \( \eta/\rho \) is the kinematic viscosity.

The viscometer is calibrated before starting the measurement of viscosities of unknown liquid. For maintaining accuracy and reproducibility of results, the viscometer is cleaned with warm chromic acid and washed several times with distilled water. Finally, the viscometer is rinsed with alcohol followed by acetone and dried under vacuum. The viscometer is initially filled with water and then time of flow of the water between two fixed marks is noted accurately with stopwatch. Similarly the
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time of flow of two more liquids of high purity and of known density and viscosity are measured. Time of flow of atleast three liquids are required to calculate $A$ and $B$ constants of the viscometer. In the present work, $A$ and $B$ constants have been determined by using double distilled water, methanol and cyclohexane. The estimated values of $A$ and $B$ are 0.0043571 and 1.7621 respectively. Once the constants of viscometer are known, the viscosity of the unknown sample can be easily estimated by measuring of time of flow of such samples. The flow time of a specified volume of liquid through the capillary was measured with a stopwatch with a resolution of $1 \cdot 10^{-2} \text{s}$. Equation 15 has been utilized to calculate the viscosity of all the pure liquids and liquid mixtures. The measurements repeated to get the concordant readings. Viscosity values are uncertain to within ± 0.001 $\text{mPa \cdot s}$.

3.6. Measurements of spectroscopic parameters

3.6.1. FT-NMR spectroscopy

$^1\text{H}$ and $^{13}\text{C}$ NMR spectra have been recorded using a JEOL AL FT NMR spectrometer operating at 300 MHz. The chemical shift, $\delta$, for all the pure liquids and liquid mixtures have been observed in the presence of CDCl$_3$ used as an external solvent.

3.6.2. FT-IR spectroscopy

Perkin Elmer (RX1) FT-IR spectrometer in the frequency range (4400-350) cm$^{-1}$ is utilized to record the FT-IR spectra. AgCl plates are used to determine the wave number, $\nu$, for all the pure liquids and liquid mixtures for all the FT-IR measurements.