CHAPTER - 7

EXPERIMENTAL PROCEDURE
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7.1 Excess Molar Volume

The majority of reliable excess volume measurements are now made with either continuous dilution dilatometers or with commercially available digital densimeters. The latter method is based on the determination of the frequency of vibration of a small tube filled with the liquid. In this method, it is necessary to take great care to ensure that evaporation losses which occur during the preparation and the transfer of the solution are kept to a minimum because the composition of the mixture has to be known to a much higher precision when compared with direct mixing methods. Also, the effect of dissolved air on the density of both the mixture and the pure components needs to be considered. In the present investigation, a continuous dilution technique has been employed for the measurement of excess molar volumes.

7.1.1 Dilatometer

A continuous dilution dilatometer of Dickinson et al. [69] type was used for the measurement of excess volumes of the binary mixtures.

Construction

The outline of the dilatometer is illustrated in Figure 7.1. 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 the dilatometer. The volume change is measured by the movement of the mercury level in the calibrated capillary $D$ which is connected via $B_{10}$ 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 by rotating a magnet over it.

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 correlations 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 amount of mercury is 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 portions are used in the construction of the dilatometer.

**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.

**Vacuum Line**

A vacuum line, consisting of a mercury diffusion pump, a rotary oil pump, a McLeod gauge and arrangements for connecting the sample holders, was used for the degasification of pure liquids. The liquid in the degasification 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.

**Working of the dilatometer**

In the continuous dilution dilatometer, stopcock $S$ is cleaned and partly greased (to avoid contact with mercury and liquids) before each filling of the dilatometer. The dilatometer is connected via the $B_{10}$ 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 up to the glass joint $E$. Care is taken that no air bubble is present within the apparatus at this or at any subsequent stage.
Figure 7.1 Dilatometer
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 \( B \) with the help of the syringe. The dilatometer is assembled as shown in Figure 1. It is clamped in a constant temperature water bath 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 glass tube \( B \) is introduced into the mixing bulb \( A \) by the hydrostatically induced flow of mercury from \( A \) to \( B \). 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 stopcock \( S \) and the mixture is stirred in the mixing bulb by the movement of the magnetic bead with a strong rotating magnet surrounding the bulb.

The number of moles of component 1 added in the bulb \( A \) is 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 volume is calculated from the change in the mercury height in the pre-calibrated capillary \( D \), using equation:

\[
V^e = C \Delta h(n_1 + n_2) \tag{7.1}
\]

where

\[
V^e = \text{excess volume, } cm^3 \text{ mol}^{-1}
\]
After determining the excess volume at one set of compositions, the dilatometer is cleaned and filled with double distilled mercury in the same manner as described earlier. The degassed component 2 is introduced in the mixing bulb $A$ and component 1 in the glass tube $B$. The whole procedure is repeated and excess volumes are calculated using Eq. 7.1.

## 7.1.2 Calculation for Excess Molar Volume

### Weight of syringe

$$\text{Weight of syringe} = a \text{ g.}$$

### Weight of syringe + solvent 1

$$\text{Weight of syringe} + \text{solvent 1} = b \text{ g.}$$

### Weight of solvent 1 added

$$\text{Weight of solvent 1 added} = (b - a)g. = W_1 \text{ g.}$$

### Molecular weight of solvent 1

$$\text{Molecular weight of solvent 1} = M_1$$

### Number of moles of solvent 1 added, $n_1$

$$\text{Number of moles of solvent 1 added, } n_1 = \frac{W_1}{M_1}$$

### Initial reading of tube length

$$\text{Initial reading of tube length} = X \text{ cm}$$

### Final reading of tube length after transferring solvent 2 in the mixing bulb from the glass tube

$$\text{Final reading of tube length after transferring solvent 2} = Y \text{ cm}$$

### Total difference in the tube length

$$\text{Total difference in the tube length} = (X - Y) \text{ cm} = L \text{ cm}$$

### Volume of solvent 2 added

$$\text{Volume of solvent 2 added} = C_2 \text{ L cm}^3 = \frac{Vol}{cm^2}$$

### Weight of solvent added, $W_2$

$$\text{Weight of solvent added, } W_2 = V \rho$$

### Molecular weight of solvent 2

$$\text{Molecular weight of solvent 2} = M_2$$

### Number of moles of component 2, $n_2$

$$\text{Number of moles of component 2, } n_2 = \frac{W_2}{M_2}$$

### Total number of moles

$$\text{Total number of moles} = n_1 + n_2$$

### Mole fraction of solvent 1

$$\text{Mole fraction of solvent 1} = \frac{n_1}{(n_1 + n_2)}$$

### Total change in height of mercury level in the capillary

$$\text{Total change in height of mercury level in the capillary} = \Delta h$$

### Excess molar volume, $V'$

$$\text{Excess molar volume, } V' = \frac{\Delta h C_2}{(n_1 + n_2)}$$
where $C_1 = 0.01033685 \text{ cm}^2$ and $C_2 = 0.924979 \text{ cm}^2$ are the calibration constants of the glass tube $B$ and the capillary $D$ respectively.

**Calculation of Density from the Excess Molar Volume Data**

The density of the binary mixture was calculated from the excess molar volume of binary mixture by the following relation:

\[
\rho_{\text{mix}} = \frac{(M_1x_1 + M_2x_2)}{V_{\text{mix}}}
\]  

(7.2)

where

\[
x_1, x_2 = \text{mole fractions of solvent 1 & 2 respectively.}
\]

\[
V_{\text{mix}} = V^E + V^{id}
\]

(7.3)

where $V^{id}$ is the ideal volume of the binary mixture and is given by:

\[
V^{id} = V_1x_1 + V_2x_2
\]

(7.4)

where

\[
V_1 = \frac{M_1}{\rho_1}
\]

(7.4a)

\[
V_2 = \frac{M_2}{\rho_2}
\]

(7.4b)

where $\rho_1$ and $\rho_2$ are the densities of the pure solvents 1 and 2 respectively.

7.2 Viscosity

7.2.1 Various Types of Viscometers

The importance of viscosity in science and technology has led to the development of numerous viscometers. Depending upon the fluid, different techniques are available for the measurement of viscosity.

Viscosity can be measured by determining:

- The time required for the flow of a definite quantity of fluid through a short tube or a capillary.
- The pressure drop through a capillary.
- The time necessary for the rise of an air bubble or the fall of a solid sphere through a liquid.
The torque required to rotate a paddle or a cylinder in the fluid.

Due to demand of accuracy, simplicity and susceptibility to mathematical treatments, there have been continuous modifications and refinements in the use of equipments for measuring viscosity.

For the determination of viscosity by successful methods, the prerequisite condition is to have laminar and streamlined flow. Depending on the fluid under consideration, there are various methods for its measurement.

**Capillary flow Viscometers**

Viscometers based on the method of capillary flow may be divided into two major classes:

- Instruments for determining relative viscosities by reference to suitable standard liquids.
- Instruments for determining absolute viscosities directly from the dimensions of the instrument and from experimental data.

Measurement of viscosity of liquid with capillary flow is most often encountered phenomenon. For determining viscosity of the fluid, the equation of laminar flow for the fluid is given by:

\[ \eta = \left[ \frac{\pi r^4 \rho t}{(8\nu (1+nr))} \right] - \left[ \frac{m \rho V}{8 \frac{(\pi (1+nr) t)}} \right] \]  

(7.5)

where

- \( r \) = radius of capillary
- \( n \) = coefficient of flow for viscometer
- \( t \) = time
- \( m \) = mass of single molecule

**Instruments to determine Relative Viscosity**

**Ostwald Viscometer:** It is usually used for comparing viscosities of different liquids. The force driving the liquid through the capillary is equal to \( h \rho g \), where \( h \) is the mean difference of level of liquid in the two limbs of the tube, \( \rho \) is the density of the liquid and \( g \) the gravitational constant. The resistance to flow depends on the
Figure 7.2 Various Types of Viscometers

- Thorpe and Rodge Viscometer
- Ostwald Viscometer
- Bingham and Jackson Viscometer

Various Types of Viscometers

- H1
- H2
- T1
- M1
- L
- M2
- R
- K2
dimensions of the capillary (which are constant) and on the viscosity of the liquid. If now, the same volume of a second liquid 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 \( h \rho \, g \). 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 outflow \( t_1 \) and \( t_2 \) for the same volume of the two liquids are in the inverse ratio, i.e.

\[
\frac{t_1}{t_2} = \frac{\eta_1}{\eta_2} / \frac{\rho_1}{\rho_2}
\]

or

\[
\frac{\eta_1}{\eta_2} = \frac{\rho_1 \, t_1}{\rho_2 \, t_2}
\]

(7.6)

This expression gives the relative viscosities of the liquids. If the absolute viscosity of one of them is known, then that of the other can be calculated.

**Variable Pressure Viscometer:** A useful form of this type of viscometer is Thorpe and Rode viscometer as shown in Figure 7.2. In this case, a measured air pressure is applied to the liquid surface in the right limb of the viscometer and the time of passage of fluid between the fixed marks is observed. Since, it is difficult to determine the viscometer dimensions with sufficient accuracy for introduction in Eq. 7.5, these are grouped into constants which are determined from flow data with liquids of known viscosity. Eq. 7.5 can be re-written as:

\[
\eta = cp \, t - C\rho / t
\]

where

\[
c = \pi \, r^4 / 8V \, (1 + nr)
\]

(7.7a)

and

\[
C = mV / 8\pi \, (1 + nr)
\]

(7.7b)

\( n \) = coefficient of flow for viscometer.

\( r \) = radius of capillary.

\( m \) = mass of single molecule with diameter \( d \) in the gaseous state.

\( V \) = volume of fluid.
**Instruments for determination of absolute viscosity**

**Bingham and Jackson Viscometer:** A simpler instrument for the determination of absolute viscosity was used by Bingham and Jackson [180] and it is shown in Figure 7.2. It is filled by means of a pipette drawn out into the left limb until the liquid reaches from $H$ to $A$, the excess overflowing into the trap. The left limb is then connected to a compressed air receiver provided with a water manometer and the time required by the meniscus to fall from $B$ to $D$ is taken. The right limb is then connected to pressure and the time from $D$ to $B$ is taken.

The time between marks for a liquid of known viscosity and density at a given pressure using the equation:

$$C = \frac{\eta + C' \rho \Delta t}{\rho \Delta t}$$  \hspace{1cm} (7.9)

Eq. 7.8a can be calculated with sufficient accuracy from the known volume between marks and the length of the capillary. $C$ is then found by observing the time between marks for a liquid of known viscosity and density at a given pressure using the equation:

$$\eta = C \rho \Delta t - C' \rho \Delta t$$ \hspace{1cm} (7.8)

**Rotational Viscometer**

If a body is rotated in a viscous fluid, a retarding force acts upon it due to viscous resistance in the fluid. If we have two coaxial cylinders separated by a viscous fluid and we rotate one cylinder with respect to other with a uniform angular velocity (if the conditions are such that fluid flow is not turbulent and there is a layer of immobile fluid in contact with each cylinder), the relation between the quantities involved is:

$$G = \frac{4\pi l a^2 b^2}{(b^2 - a^2)\eta \tau}$$ \hspace{1cm} (7.10)

$G$ = angular velocity

$a$ = radius of inner cylinder

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\[ b = \text{radius of outer cylinder} \]

\[ \tau = \text{torque required to rotate a cylinder} \]

Coutte's Viscometer is an example of rotational viscometer. With such kind of instruments, dimensions can be measured directly or determined collectively as an instrumental constant from calibration with liquids of known viscosity. The dimensions being known, the viscosity may be calculated from observation of \( G \) and \( \tau \) which are measured in different ways. Torsion wires, springs, dead weights and electrical measurements of torque have all been used in this connection. Various viscometers have been designed on this principle.

**Falling Body Type [180]**

It is based on the well-established accurate hydrodynamic law i.e. Stokes’s law for the terminal rate of fall (\( v \)) of a sphere (radius \( r \), density \( \rho_1 \)) through a liquid (density \( \rho_2 \)), namely:

\[
v = \frac{2}{9} \left[ (\rho_1 - \rho_2) \right] \frac{r^2 g}{\eta} \tag{7.11}
\]

In the falling-sphere viscometer a ball-bearing is timed in falling a measured distance through a cylindrical tube of liquid. Corrections are needed, however, for the influence of the walls and bottom of the tube. The former is usually quite important, it can be allowed for approximately by introducing a factor of \((1 + 2.1 \frac{r}{R})\) below the line of the right hand side of Stokes’s law (\( R = \text{radius of tube} \)). Here again relative determinations with the same tube and ball largely eliminate these complications. The method is particularly suitable for viscous oils which are available in quantity. The simple apparatus of Gibson and Jacobs [40] is suitable.

**7.2.2 Experimental Method**

The apparatus used to determine the viscosity was kept in constant temperature bath (Type MK 70, MLW, Germany) for about half an hour before any observation was made. The temperature was controlled to an accuracy of \( \pm 0.02^\circ K \).

In the present work, viscosity was determined using Ubbelohde suspended level viscometer, which is a glass capillary viscometer, as shown in Figure 7.3. Ubbelohde's viscometer consists of three limbs connected to a bulb \( d \). The central
limb is essentially a pipette with two marks $M_1$ and $M_2$ and a capillary $c$ through which the liquid contained in bulb $b$ flows under gravity into the bulb $d$. The central limb is closed at the top with the help of a cap $S_1$ and the other two limbs are connected at the top and closed by cap $S_2$.

**Filling and working of Viscometer:** The viscometer was cleaned with warm chromic acid solution followed by washings with distilled water and with acetone. After drying it under vacuum, it was rinsed and filled with the liquid whose time of flow was to be found. To fill the liquid in the viscometer, the cap $S_2$ is removed and the liquid is filled in the bulb $d$. After filling, the cap $S_1$ is removed and cap $S_2$ is placed back at its position. Then the viscometer is inverted and the liquid rises in all the three limbs. Sufficient liquid is to be taken so that liquid in central limb fills bulb $a$ and $b$ completely and care is to be taken that there should be no air bubbles entrapped in the viscometer. The viscometer is then brought back to its original position and then placed in constant temperature bath for attaining the desired temperature. To achieve the constancy of the hydrostatic head of the liquid and the same alignment of the capillary, it was put properly in the rubber groove and was clamped gently at the top after immersing to an appropriate depth in the water thermostat, maintained at the required temperature. When the temperature of the water thermostat was constant for nearly 30 minutes, the time of flow of liquid, $t$, between the two fixed marks $M_1$ and $M_2$ was noted with the help of an electronic stop watch with an accuracy of ±0.01 sec. The measurements were repeated to get three concordant readings.

The viscosity at a particular temperature is calculated using the following simplified relation given by Martin [48]:

$$\nu = \eta / \rho = A t + B / t$$  \hspace{1cm} (7.12)

where $\nu$ = kinematic viscosity
$\eta$ = dynamic viscosity
$\rho$ = density
$A$, $B$ = viscometer constants
Figure 7.3 Ubbelohde Viscometer
Evaluation of Viscometer Constants

The constants $A$ and $B$ of Eq. 7.12 were evaluated from measured efflux times and densities of two or more purified liquids of known density and viscosity.

At a particular temperature, two equations for two samples are as follows:

\[ v_1 = \frac{\eta_1}{\rho_1} = A_1 \frac{t_1}{t_1} + B/t_1 \]  
\[ (7.12a) \]

\[ v_2 = \frac{\eta_2}{\rho_2} = A_2 \frac{t_2}{t_2} + B/t_2 \]  
\[ (7.12b) \]

7.3 Ultrasonic Velocity

Ultrasonic velocity measurements stand as one of the primary techniques for study of properties of matter such as mechanical, electromagnetic and particle interaction. The propagation of high frequency stress wave 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 velocity and attenuation can be determined by two standard techniques:

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

The pulse echo method overcomes almost all the limitations of the continuous wave 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 bounded to the specimen. The ultrasonic pulse travels though the sample and an echo is registered each time it returns to the transducer. The amplitude of successive echoes decreases exponentially due to attenuation in the sample. In general, the amplitudes are related by:

\[ A_2 = A_1 e^{-dx} \]  
\[ (7.13) \]

where $A_1$ and $A_2$ are the amplitude of echoes and $x$ is the attenuation coefficient. For measuring the velocity of ultrasonic waves, time elapsed between registering of $A_1$ and $A_2$ i.e. $\tau$ is to be measured accurately. Then velocity $u$ of the sample is given by:

\[ u = \frac{d}{\tau} \]  
\[ (7.14) \]
where $d$ is the distance travelled by ultrasonic waves in registering the two echoes ($d = 0.0175503 \, m$).

7.3.1 Experimental Setup

Interferometer UTI-101: The ultrasonic velocity measurements were done with the help of interferometer UTI-101. The experimental set up consist of the three components: the ultrasonic velocity measuring cell, time intervalometer and Oscilloscope.

The sample is put in the cell where the waves are produced and reflected by means of transducer. The signals are adjusted and peaks are overlapped on the oscilloscope while time intervalometer gives the time period $(t)$ of echo. Oscilloscope is the simplest equipment by which one can measure both attenuation and velocity. Out of sing around system, pulse-echo overlap method and pulse super-position method, the pulse echo overlap method 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 measurements 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 gaining changes including the attenuation changes in the sample.

7.3.2 Method of Measurement

To make 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 continuous wave 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. Only intensified peaks are considered and main pulse delay is adjusted so that signals are in the centre of the screen. The frequency is adjusted so that the signals overlap each other. The value is found for each dilution of the sample solution and the same procedure is followed every time.
Figure 7.4 Interferometer (UTI – 101)