EXPERIMENTAL

CHAPTER 3
EXPERIMENTAL

This chapter deals with specifications of the chemicals, methods of their purification and test of their purity. It also includes the experimental techniques used for measuring excess heat capacity and excess volume.

3.1 Chemicals and their sources:
The sources and grades of the chemicals used in present work are listed in table 3.1

Table 3.1 Sources and grades of chemicals

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Source</th>
<th>Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>•Ethylbenzene</td>
<td>Fluka AG, Buchs</td>
<td>Pure</td>
</tr>
<tr>
<td></td>
<td>Fluka AG, Switzerland</td>
<td></td>
</tr>
<tr>
<td>o-Xylene</td>
<td>Sisco-Chem Industries, India</td>
<td>Pure</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>Fluka AG, Buchs, Switzerland</td>
<td>Pure</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>Sisco-Chem Industries, India</td>
<td>Pure</td>
</tr>
<tr>
<td>Nonane</td>
<td>Sisco-Chem Industries, India</td>
<td>Pure</td>
</tr>
</tbody>
</table>
3.2 Purification of the chemicals used:

(a) Ethylbenzene

Thiophene from ethylbenzene was removed by shaking concentrated sulphuric acid, then allowed to stand for some time. A yellow layer separated out at the bottom was removed. Repeated the same procedure several times until no yellow colour was imparted to sulphuric acid. Ethylbenzene was washed several times with distilled water and then with sodium bicarbonate solution, followed by distilled water again. Residual water was removed from ethylbenzene by keeping it over anhydrous calcium chloride for overnight. The last traces of water were removed by the distillation of ethylbenzene with sodium metal. The middle fraction distilling at 403.3 K was collected and stored over molecular sieves (4 Å) for further use.

(b) o-Xylene

o-xylene was treated with concentrated sulphuric acid to check the presence of thiophene. Since no yellow colour was detected, this ensured the absence of thiophene. It was distilled over sodium metal and middle fraction of second distillate at 417.5 K was collected and stored for further use.

(c) m-Xylene

Traces of thiophene were found in our sample of m-xylene too. Same procedure was adopted for removal of thiophene as for ethylbenzene. Thiophene free m-xylene was stored over anhydrous calcium chloride for overnight. Last
traces of moisture were removed by fractional distillation over sodium metal. The middle fraction at 412.3 K was collected and stored over molecular sieves (4 Å).

(d) p-Xylene

Having ensured that p-xylene was free from thiophene, it was recrystallized 4-5 times in a freezing mixture and the mother liquor was decanted off. p-Xylene was distilled over dry sodium metal and the middle fraction was collected at 411.4 K and stored over molecular sieves for further use.

(e) Nonane

Nonane was kept over magnesium sulphate for 36 hours to remove moisture from it. Then it was distilled over sodium metal and middle fraction distilling at 423.9 K was collected and stored for further use.

The purity of the chemicals was checked by determining their densities. These densities were compared with the best available literature values\(^{59,60}\) and the agreement was found to be good. The experimental and the literature values are listed in table 3.2.
Table 3.2 Densities of pure components at 298.15 K

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Density/(gm cm(^{-3}))</th>
<th>Experimental</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylbenzene</td>
<td>0.86272</td>
<td>0.86264(^{(a)})</td>
<td></td>
</tr>
<tr>
<td>o-Xylene</td>
<td>0.87583(^{(b)})</td>
<td>0.87583(^{(b)})</td>
<td></td>
</tr>
<tr>
<td>m-Xylene</td>
<td>0.85990(^{(a)})</td>
<td>0.85990(^{(a)})</td>
<td></td>
</tr>
<tr>
<td>p-Xylene</td>
<td>0.85670(^{(b)})</td>
<td>0.85670(^{(b)})</td>
<td></td>
</tr>
<tr>
<td>Nonane</td>
<td>0.71381(^{(a)})</td>
<td>0.71381(^{(a)})</td>
<td></td>
</tr>
</tbody>
</table>

(a) Reference 59
(b) Reference 60

3.3 Heat capacity measurements:

C-80 calorimeter (SETARAM, FRANCE) was used to determine the heat capacities of pure components and excess molar heat capacities of various binary mixtures. The Calorimeter consists of the following units:

(a) Calorimetric unit
(b) Temperature programmer/controller
(c) Amplifier
(d) Recorder

3.3.1 Calorimetric unit:

The calorimeter is in the form of a vertical cylinder on a rectangular base. It is made of aluminium and with two holes in which two calorimetric vessels can be fitted.
tightly for proper thermal contact. These two holes providing housing for two experimental vessels, (the measurement and reference vessels) are surrounded by a series of thermocouples. These thermocouples connected in series are called fluxmeters (Figure 3.1). The thermal equilibrium between the vessels can be disturbed by:

(i) Simultaneous heating of the vessels and the heat capacity of the vessels is different due to their contents.

(ii) Due to some physical or chemical process taking place in the sample vessel.

Calorimetric vessels are made as identical as possible by having same shape, size, dimensions and material of fabrication. These can be stabilized at desired temperature. If one vessel is taken empty and other is filled with liquid, their heat capacities are quite different. Thus on heating a temperature difference is created generating a temperature gradient. The heat exchange will continue to take place until both the vessels have attained the constant temperature.

3.3.2 Temperature programmer/controller:

Temperature programmer and controller controls the temperature of the calorimeter by means of a platinum resistance probe which by means of a transducer drives the power through a transformer into the heating elements. The programmer module generates a linearized electrical signal which follows the temperature programme. The thermal output shows the quantity of heat necessary for the temperature
FIG. 3.1 C-80 CALORIMETER (INTERNAL VIEW)
variation.

3.3.3 Amplifier:

It amplifies the low DC signal from calorimeter linearly and has very low noise. It gives an output voltage of ±1 V which can be fed into analog strip chart recorder, or a digital voltmeter/computer.

3.3.4 Recorder:

The recorder having two pen measures the heat flux signal and the temperature of the calorimetric block. The recorder is connected to the calorimeter through the amplifier. The speed of paper can be adjusted depending on the mixture and the temperature range.

3.3.5 Calorimetric vessel:

It is a long cylindrical vessel (80 mm height and 17 mm diameter) on the top of which a long capillary having a length of 280 mm is welded (Figure 3.2).
The vessel, made of stainless steel has capacity of about 16 ml. The vessel is filled with the desired liquid by means of a syringe fitted with a teflon capillary. The accuracy in the measurement of heat capacity of a liquid depends on the corrective term due to the vapour phase above the liquid. In order to overcome this difficulty, a special calorimetric vessel was used. The junction of the tube and capillary vessel is so welded and machined that there is no vapour or bubble retained in the experimental vessel. When the liquid is heated, the liquid expands freely in the tube, but the volume of the liquid in the vessel, located in the detection zone of the calorimeter remains constant. Two vessels are introduced in the calorimeter, we have called, the vessel in front of the instrument as the "sample vessel" and the one towards the rear as the "reference vessel" and are used as such.

3.3.6 Working principle of the calorimeter:

Two experimental vessels are placed in the calorimetric block which imposes the temperature of the experiment as fixed or variable. Two symmetrical thermal fluxmeters composed of thermocouples connected in series surround the experimental vessels and thermally connect them to the calorimetric block. They give out an electrical signal which represents the thermal exchanges between the vessels and calorimetric block. The instrument can be used in the following two manners:
3.3.6(a) Continuous fluxmetric measurements at constant temperature:

If one vessel is the source of a continuous and constant power \( W \), this power will flow through the thermocouples into the calorimetric block. (Figure 3.3(a)) The various temperatures will be constant as long as the power \( W \) is constant. If one of the thermocouples \( i \) transfers the elementary power \( w_i \), there is a very small difference in temperature between the internal and external junctions.

\[
w_i = k_i \delta \theta_i \tag{3.1}
\]

Where \( k_i \) is thermal conductance (Figure 3.3(b)). \( \delta \theta_i \) is small temperature difference.

This small difference generates an e.m.f.:

\[
e_i = \epsilon_i \delta \theta_i \tag{3.2}
\]

Where \( \epsilon_i \) is the thermoelectric value of the thermocouple.

\[
e_i = \left[ \frac{\epsilon_i}{k_i} \right] w_i \tag{3.3}
\]

Since all the thermocouples are connected in series, the total e.m.f. produced is:

\[
E = \Sigma e_i \tag{3.4}
\]

corresponding to the power \( W \) transferred.

\[
W = \Sigma w_i \tag{3.5}
\]

\[
E = \Sigma \left[ \frac{\epsilon_i}{k_i} \right] w_i \tag{3.6}
\]
As all the thermocouples are identical, they have the same thermal conductance and same thermoelectric constant $\varepsilon$. Therefore:

$$E = \frac{\varepsilon}{k} \sum w_i$$

$$= \frac{\varepsilon}{k} W$$

or

$$W = A E \quad (3.7)$$

Where $A$ is calibration constant. Therefore electric signal is proportional to power. If the power $W$ varies with time, the e.m.f. signal varies proportionally. The construction of the fluxmeter is such that heat conductance, other than due to the thermocouples is negligible.

3.3.6(b) Variable fluxmetric measurement at constant temperature:

Initially the experimental vessel and fluxmeter can be represented by a heat capacity $C$ and conductance $k$ connecting the vessel to the calorimetric block at a constant temperature $\theta_0$. If $W$ is the power generated in the vessel, $w$ is the power exchanged by the fluxmeter, $\Delta \theta$ is the temperature difference between the vessel and calorimetric block (Figure 3.3(c)), the system follows the equation:

$$W = w + C \frac{d\theta}{dt} \quad (3.8)$$

Where $\theta = w/k$

$$W = w + \left( \frac{C}{k} \right) \frac{dw}{dt} \quad (3.9)$$

and time constant $T = C/k \quad (3.10)$
As the thermal fluxmeter delivers a signal proportional to the exchanged power \( W \), the relationship between the power generated in the vessel and the electric signal is:

\[
W = A \left( E + T \frac{dE}{dt} \right)
\]  
\[(3.11)\]

The instrument response to instantaneous power pulse and graded power is shown in figures 3.3 (d) and 3.3 (e) respectively.

3.3.6(c) Variable temperature of calorimetric block compensation through symmetrical increase:

If due to residual instability of the regulator or to the temperature \( \theta_0 \) of the calorimetric block changes, the vessel follows the change and move towards \( \theta_0 \). The variation in temperature requires thermal power which is transmitted by the fluxmeter. It produces a disturbing signal which can be greater than the signal produced by the experiment, especially in a programmed mode. To reduce the disturbing signal, the C-80 calorimeter is fitted to a second vessel with identical features which is surrounded by a second fluxmeter.

3.4 Procedure for the measurement of the heat capacity of a liquid:

Initially, both the reference as well as the sample vessels were kept empty. The calorimeter was allowed to stabilize so that there was no variation in the signal for a long time. After this the temperature was raised in a programmed manner; and the deviation of the two empty cells
FIG. 3.3 PRINCIPLE OF C-80 CALORIMETER
(reference and sample) was recorded. The area under the calorimetric curve \( Q_0 \) was determined by counting the small squares, which is proportional to the heat necessary for the temperature variation.

At the second stage, the sample vessel was filled with a standard liquid (p-xylene), heated by step heating mode and the area under the calorimetric curve \( Q_1 \) was determined. Finally, the sample vessel was filled with the liquid whose heat capacity is to be determined and the area under the calorimetric curve \( Q_2 \) was determined (Figure 3.4).

The measurement of heat capacity of a liquid needs accurate value of area under the curve. Unfortunately, the repeated experiments showed that the results were not reproducible. After a number of experiments, it was concluded that irreproducibility was due to spikes in the main supply, which affected the working of the programmer. The instrument is very sensitive to these or power failure even for \( 10^{-4} \) second. Therefore, it was necessary to procure an uninterruptible power supply (U.P.S.). The U.P.S. consists of four 12 V batteries which are a source of power to an inverter and supplies electricity at 230 V AC (50 Hz). The batteries are charged continuously and are automatically cut off, when they get fully charged. If the main supply goes off, the calorimeter functions normally by supply from U.P.S. for half an hour. After the installation of U.P.S., the calorimeter functioned very well and reproducibility and accuracy was established by measuring the heat capacities of several pure liquids.
Fig. 3.4 Calorimetric Curve (Direct)
3.5 Excess heat capacity:

The heat capacities of a number of liquids and liquid mixtures was determined by the equation:

\[ C^E_{P,m} = C^0_{P,m} - [(1-x)C^0_{P,m1} + xC^0_{P,m2}] \] (3.13)

Where \( x \) is the mole fraction of second component. \( C^0_{P,m1} \) and \( C^0_{P,m2} \) are molar heat capacities of first and second component respectively.

3.6 Density measurements:

Densities of pure components and the various binary mixtures at different mole fractions and temperatures have been measured with the help of a bicapillary pyknometer.

3.6.1 Construction of pyknometer:

The pyknometer was fabricated from the uniform bore capillary, which was blown as a bulb of about 9 ml. capacity in the middle. The capillary on the either side of the bulb was bent at right angles and the limbs were kept parallel to each other. One of the limbs was slightly bent near the top to distinguish it from the other. A nichrome wire was attached to the limbs to hold the pyknometer. Reference marks \( M_1 \) and \( M_2 \) were etched on the two limbs of the pyknometer (Figure 3.5).

3.6.2 Calibration of capillary:

The bore of the capillary used for the construction of pyknometer was calibrated by measuring with a travelling microscope, the length of a known weight of mercury thread.
FIG. 3.5 BICAPILLARY PYKNOMETER
The capillary having uniform bore was selected for the construction of pyknometer.

3.6.3 Calibration of pyknometer:

The volume of the pyknometer bulb up to fixed marks was determined by weighing in it freshly distilled mercury. The temperature was maintained and the position of mercury thread in two limbs was measured with the help of a cathetometer. Mercury contained in the pyknometer was weighed and the volume of the pyknometer up to fixed marks \( M_1 \) and \( M_2 \) was calculated from the volume of capillary above or below the fixed marks and density of mercury at the required temperature.

3.6.4 Working procedure:

The pyknometer after thorough cleaning and drying was accurately weighed on an electric balance. It was filled with the desired solution using a hypodermic syringe. Care was always taken to avoid any air bubble being entrapped in the liquid. The pyknometer was reweighed after wiping it's outer surface. It was then clamped into a water thermostat maintained at desired temperature. The pyknometer was kept in vertical position with the help of clamps. After the desired temperature had been stabilized for about half an hour, the length of liquid columns above or below the fixed marks \( M_1 \) and \( M_2 \) were read with the help of a cathetometer. This volume was added or subtracted from the standard volume of the pyknometer. The pyknometer was taken out from the thermostat, wiped clean and dried with a tissue paper and weighed again to ascertain the final weight of the liquid.
3.6.5 Thermostat for pyknometer:

A water thermostat of brass with a glass window on the front side of it was fabricated. This was further surrounded by a wooden box and the gap between the two was filled with insulating material. The temperature control was achieved by using an efficient stirring device, immersion type heating rod, a toluene regulator and an electronic relay. The temperature control was better than ±0.005 K which was monitored on a Beckmann thermometer.

3.6.7 Excess molar volume:

Excess molar volume is obtained from density measurements using the equation:

\[ \Delta V^E_m = \frac{[(1-x)M_1 + xM_2]}{\rho_m} - \frac{[(1-x)M_1]}{\rho_1} - \frac{xM_2}{\rho_2} \]

(3.14)

Where \( x \) is mole fraction of component 2. \( \rho_m, \rho_1, \rho_2 \) are the densities of mixture, pure components 1 and 2 respectively.