CHAPTER II
MATERIAL AND METHOD
LIQUIDS AND THEIR PURIFICATION

Aniline
Aniline (B.D.H. AR grade) was doubly distilled after adding some zinc dust as suggested by Vogel\(^1\) and then stored in amber coloured bottles.

1,2-Dichloroethane
(B.D.H. AR grade) 1,2-dichloroethane was first washed with five percent sodium carbonate solution and then with water. The liquid was then dried over anhydrous calcium chloride and distilled.

Pyridine
Pyridine (B.D.H. AR grade) was refluxed\(^2\) over potassium hydroxide pellets for 5-7 hours and then distilled with careful exclusion of moisture.

Picolines
\(\alpha\)-Picolines and \(\gamma\)-picoline (B.D.H. AR grade) were purified\(^3\) in a manner analogous to that for pyridine.

n-Heptane and n-hexane
n-Heptane and n-hexane (B.D.H. AR grade) were treated\(^4\) with 10 percent of the volume of concentrated sulphuric acid followed by shaking with successive portions of a concentrated solution of potassium permanganate in 10 percent sulphuric acid until the colour of the permanganate remains unchanged. The liquids were then thoroughly washed with water, dried over
anhydrous calcium chloride, distilled and then stored over sodium wire.

The purity of the purified compounds was checked by measuring their density at 293.15 ± 0.01 K. The results are reported below and have been compared with their corresponding literature values.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Density (gm cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental value</td>
</tr>
<tr>
<td>n-heptane</td>
<td>0.68374</td>
</tr>
<tr>
<td>n-hexane</td>
<td>0.65936</td>
</tr>
<tr>
<td>Aniline</td>
<td>1.02170</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>1.25292</td>
</tr>
<tr>
<td>Pyridine</td>
<td>0.98257</td>
</tr>
<tr>
<td>α-picoline</td>
<td>0.94429</td>
</tr>
<tr>
<td>γ-picoline</td>
<td>0.95485</td>
</tr>
</tbody>
</table>

**Measurement of molar excess volumes**

The dilatometer, which has been used here for measuring molar excess volumes for binary as well as ternary mixtures of non-electrolytes is a modified version of the dilatometer used by Brown and Smith and is described below.

(a) **Description of the dilatometer:**

The dilatometer is shown in Fig. 3.1. It consists of two limbs having a vacuum tested B-7 standard joint at one end and two bulbs B and C of different capacities at the other end.
FIG. 3.1. DILATOMETER FOR MOLAR EXCESS VOLUMES
These limbs are interconnected through a small bent tubing. A capillary of thin uniform bore, with a reference mark R, is fused to the side of the compartment A as shown in Fig. 3.1.

(b) **Experimental procedure for** $V_{ij}^E$

A small amount of mercury (2-5 ml) was taken in the dilatometer and weighed. One of the degassed liquids say (i) was added to the bulbs B and/or C with the help of a hypodermic syringe (having a long 9 inches needle at its end) in such a way that no air bubbles were entrapped in these bulbs. The dilatometer was weighed again and the second degassed liquid was added to the side A and/or C and then stoppered keeping the liquid level in the capillary at a suitable position. The dilatometer was then placed in a thermostatic bath (controlled to ± 0.01 K by a mercury-in-toluene regulator). The position of the reference mark and that of the liquid level in the capillary was noted with the help of a cathetometer (manufactured by M/s OSAW, Ambala) which could read to ±0.001 cm. After the attainment of thermal equilibrium, the contents of the dilatometer were mixed by tilting it gently sideways for several times to ensure thorough mixing. The position of the reference mark and that of the liquid in the capillary was again noted after waiting for some time to enable the mixture to attain the temperature of the thermostatic bath. The molar excess volumes, $V_{ij}^E$, for binary (i+j) mixtures were then calculated from the expressed

$$V_{ij}^E = \pi r^2 \Delta h/(n_i + n_j) \quad \ldots (1)$$
where

\[ r = \text{radius of capillary,} \]

\[ \Delta h = \text{change in liquid level in the capillary on mixing,} \]

and

\[ (n_1 + n_j) = \text{total number of moles of the (i+j) mixture.} \]

Molar excess volumes for ternary (i+j+k) mixtures were determined in exactly the same manner as that described for the binary mixture except that the three components 1, j and k were now taken in the three compartments A, B and C and the molar excess volumes for these mixtures were computed from the relation

\[ V_{ijk}^E = \pi r^2 \Delta h (n_1 + n_j + n_k) \quad \ldots (2) \]

where

\[ r = \text{radius of the capillary,} \]

\[ \Delta h = \text{change in the level of liquid in the capillary on mixing,} \]

and

\[ (n_1+n_j+n_k) = \text{total number of moles of the (i+j+k) mixture.} \]

Sources of error

The measured \( V^E \) values are subjected to the following sources of errors.

(1) Instrumental errors

Equation (1) can be written as

\[ V_{ij}^E = \left( \frac{w}{\rho \cdot 1} \right) \Delta h (n_1 + n_j)^{-1} \quad \ldots (3) \]

where \( w \) is the weight of mercury having length equal to 1 cms and \( \rho \) is the density. The error in \( V^E \) would then be due to error in the measurement of \( w, \rho, 1, \Delta h \) and \( (n_1 + n_j) \).
From equation (3), it follows that

\[
\left(\frac{dV^E_{ij}}{V^E_{ij}}\right) \times 100 = \left[\frac{dw}{w} - \frac{d\rho}{\rho} - \frac{dl}{l} + \frac{d\Delta h}{\Delta h} - \frac{d(n_i + n_j)}{(n_i + n_j)^2}\right] \times 100
\]

Equation (4) thus gives the percentage error in the \(V^E_{ij}\) values and can be determined by substituting the various values in this equation. For a typical 1,2-dichloroethane (i) + pyridine (j) mixture at \(x_i = 0.4982\) at 298.15 K the various uncertainties in \(w, l, \rho, \Delta h\) etc. are

- \(dw = 0.0001\) g
- \(dl = 0.0001\) cm
- \(d\rho = 0.00005\) g cm\(^{-3}\)
- \(d(\Delta h) = 0.001\) cm
- \(d(n_i + n_j) = 0.0001\) mole

\(w = 0.2981\) g
\(l = 11.1210\) cm
\(\rho = 13.53400\) g cm\(^{-3}\)
\(\Delta h = 0.0484\) cm
\(\Delta T = 0.01\) K

so that the total error in \(V^E\) due to uncertainties in \(w, l, \rho, \Delta h\) etc. comes out to be \(\pm 0.5\%\).

For a ternary (i+j+k) mixture equation (2) can be expressed as

\[
V^E_{ijk} = \left(\frac{w}{\rho l}\right) \Delta h (n_i + n_j + n_k)^{-1}
\]

so that

\[
\frac{dV^E_{ijk}}{V^E_{ijk}} \left[\frac{dw}{w} - \frac{d\rho}{\rho} - \frac{dl}{l} - \frac{d\Delta h}{\Delta h} - \frac{d(n_i + n_j + n_k)}{(n_i + n_j + n_k)^2}\right] \times 100
\]

\(\cdots(6)\)
expresses the percentage error in the measured molar excess volumes for the ternary system in terms of the uncertainties in the values for \( w, \rho, l, \Delta h \) and \( (n_i^n + n_j^n + n_k^n) \). For typical 1,2-dichloroethane \((i) + \) pyridine \((j) + \alpha\)-picoline \((k)\) mixture at \( x_i = 0.2914, x_j = 0.3492 \) \( (x_i \) and \( x_j \) are the mole fractions of components \( i \) and \( j \)) at 298.15 K the uncertainties in \( w, \rho, l, \Delta h, (n_i^n + n_j^n + n_k^n) \) are given below:

\[
\begin{align*}
dw &= 0.0001 \text{ gm} \\
dl &= 0.001 \text{ cm} \\
d\rho &= 0.0005 \text{ gm cm}^{-3} \\
d(\Delta h) &= 0.001 \text{ cm} \\
d(n_i^n + n_j^n + n_k^n) &= 0.0001 \text{ mol} \\
w &= 0.2485 \text{ gm} \\
l &= 9.089 \text{ cm} \\
\rho &= 13.53400 \text{ gm cm}^{-3} \\
\Delta h &= 2.681 \text{ cm} \\
(n_i^n + n_j^n + n_k^n) &= 0.0201 \text{ mol} \\
\Delta T &= 0.01 \text{ K}
\end{align*}
\]

The total error in \( V^E \) due to all these uncertainties comes out to be \( \pm 0.55\% \).

(ii) **Errors due to evaporation**

The \( V^E \) values are also subjected to the errors due to evaporation of the liquid from the capillary. However, \( V^E \) values for benzene + cyclohexane mixture showed a negligible deviation \( (\pm 0.0005 \text{ cm}^3 \text{ mol}^{-1}) \) from the values reported for this mixture by Marsh \(^{12} \).
(iii) **Errors due to change in area of cross-section of capillary**

Change in temperature can also affect the internal area of cross-section of the capillary at a temperature far removed from calibration temperature. An analysis of the results has shown that the error due to this cause is negligible.

The reliability of the dilatometer was checked by determining $V_{ij}^E$ for (benzene + cyclohexane) mixture at 298.15 K and these values agreed well with the best values reported for this mixture by Marsh\textsuperscript{12} (see Fig. 3.2).

**Measurements of molar excess enthalpies**

The calorimeter which has been used for measuring molar excess enthalpies is described below:

**Description of the calorimeter**

The calorimeter is shown in Fig. (3.3). It consists of a double walled glass mixing vessel having a vacuum tested B-12 standard joint at one end and two bulbs (A and B) of different capacities at the other end. The liquid components are separated over mercury taking care to avoid any vapour space in the limb (A') and the two bulbs A and B. The outer jacket can be evacuated through vacuum stop cork (x). A side tube with capillary 'C' and bulb 'O' is fused in the middle of mixing cell. A part of capillary is filled with mercury to prevent the liquids from coming in contact with atmosphere. This capillary provides an air space which ensures that the volume change during mixing causes no change of pressure. The calorimeter heater (resistance = 14.622 $\Omega$) is made of constantan wire wound round a glass tube fused with the B-12
FIG. 3.2. Molar excess volumes $V_E$ of cyclohexane (i) + benzene (j) at 298.15 K.

- Literature value
- Present work
Fig. 3.3. Calorimeter for He measurements.
joint. A thermistor (resistance = 200 Ω) is passed through the glass tube to record changes in temperature. The thermistor was enclosed in a thin steel capsule and the space between the thermistor and the capsule is filled with mercury to make it a good conductor of heat.

**Electrical circuit**

The whole assembly consisted of two electrical circuits:

1. Heating circuit
2. The thermistor circuit

The heating circuit is shown in Fig. (3.4). It consists of a 6 volt battery 'B' connected to a milliammeter 'A', one ohm standard resistance 'S' and a heater 'H' through a key 'K'. The two terminals of the standard resistance are connected to a vernier potentiometer (which could read to ± 0.00001 V) to measure the magnitude of the current in the circuit accurately.

The thermistor circuit is a Wheatstone's bridge made up of two adjustable resistances P and Q, a thermistor (200 Ω) and a standard resistance and is shown in Fig. (3.5).
The bridge is supplied with current from a stabilized power supply (1.5 volt) and the unbalanced current is monitored on a digiscribe recorder (No. 5220480 manufactured by M/s Digital Electronics Ltd., Bombay in collaboration with Houston Instruments, a Division of Bausch and Lomb.

**Experimental procedure for $H^E$ for (i+1) mixtures:**

An appropriate amount of mercury was placed in the calorimeter which was then weighed. One of the degassed liquids say (1) was added to the bulb A and/or B with the help of a hypodermic syringe (having a 9 inches needle at its neck) ensuring that no air bubbles were entrapped in the bulbs and the calorimeter was reweighed. The second degassed liquid j was then taken in the compartment, A' and the stopper was replaced so that mercury level in the capillary was at a suitable position. The calorimeter was again weighed and then placed in a thermostatic bath whose temperature was controlled to better than $\pm 0.01$ K by a mercury-in-touene regulator. The contents were allowed to attain thermal equilibrium. The outer jacket was then evacuated. A digiscribe recorder (No. 5220480 manufactured by M/s Digital Electronics Ltd., Bombay in collaboration with Houston Instruments, a Division of Bausch and Lomb) at $0.001$ vol/cm sensitivity and a chart speed of $50$ mm/mt was then switched on after about half an hour. After the appearance of a stable base line, the liquid components were then mixed by tilting the calorimeter by about $60^\circ$ from the vertical by an automatic machine and an appropriate current was passed through the calorimeter heater for compensation (for endothermic reactions only) and the time of passage was noted with
the help of an electronic counter timer (type 701, M/s Spstronics, Ahmedabad capable of reading correct to ± 0.0001 sec). When the slope of the line attained a constant value, current was again passed for calibration and the time of heating was adjusted to get approximately the same peak height as in the case of compensation. The recorder was switched off when the slope of the second peak was also constant. The molar excess enthalpy was calculated by the relation

$$H_{ij}^E = \frac{C^2 R t_1 - C^2 R t_2}{\Delta h_2} \frac{\Delta h_1}{(n_1 + n_j)}$$

...(7)

where $C$ is the current in amperes, $R$ is the resistance of the calorimeter heater in ohms, $t_1$ is the time for which the current was passed for compensation, $t_2$ the time for which the current was passed for calibration, $\Delta h_1 / \Delta h_2$ is the factor used to calculate the amount of heat required for exact compensation.

$\Delta h_1$ and $\Delta h_2$ have the same significance as described by Adock and McGlashan. In the case of exothermic reactions, since $t_1$ becomes zero, $H_{ij}^E$ is then given by

$$H_{ij}^E = - \frac{C^2 R t_2}{\Delta h_2} \frac{\Delta h_1}{(n_1 + n_j)}$$

...(8)

Molar excess enthalpies for ternary (i+j+k) mixtures were obtained in exactly the same manner as that described for the (i+j) mixtures except that the three i, j and k components were taken in the three compartments. Molar excess enthalpies for the (i+j+k) mixtures were then calculated from the relation

$$H_{ijk}^E = \frac{C^2 R t_1 - C^2 R t_2}{\Delta h_2} \frac{\Delta h_1}{(n_1 + n_j + n_k)}$$

...(9)

(for endothermic reactions)
\[
H^E_{ijk} = -C^2Rt_2 \frac{\Delta h_1}{\Delta h_2}/(n_1+n_j+n_k)
\]  

(for exothermic reactions)

where \( C, R, t_1, t_2, \Delta h_1, \Delta h_2 \) have the same significance as that described for the \((i+j)\) binary mixtures.

Sources of error

Excess enthalpy measurements are subjected to following errors:

1. **Instrumental error**
   
   This error can be determined easily as for binary \((i+j)\) mixtures we have
   \[
   H^E_{ij} = (C^2Rt_1 - C^2Rt_2 \frac{\Delta h_1}{\Delta h_2})/(n_1+n_j)
   \]
   and putting
   \[
   C^2Rt_1/(n_1+n_j) = A
   \]
   and
   \[
   C^2Rt_2(\frac{\Delta h_1}{\Delta h_2}) n_1+n_j = B
   \]

   the percentage error in \( H^E \) was calculated by considering the errors in \( A \) and \( B \), which were estimated by considering the errors in the individual quantities, \( C, R, t_1, t_2, \Delta h_1, \Delta h_2 \) and \((n_1+n_j)\). The total percentage error in \( H^E \) for binary \((i+j)\) as well as ternary \((i+j+k)\) mixtures was found to be about \(\pm 1.0\) percent.
(ii) Errors can also arise due to the inefficient control of temperature.

(iii) The leakage of heat along the heater and thermistor wires on account of difference of temperature on mixing constitute another source of error for the measured $H^E$ values.

The working of calorimeter was checked by measuring molar excess enthalpies for carbon tetrachloride + benzene mixtures at 298.15 K and these agreed well within the experimental uncertainties (which is ± 1.0 percent here) with the best literature values\textsuperscript{14} (see Fig. 3.6).

Molar excess Gibbs free energies

The apparatus used to compute molar excess Gibbs free energies for binary mixtures is discussed below:

Description of the apparatus

The apparatus is shown in Fig. (3.7). It consists of a flask A having a B-24 standard joint at its neck at B and a side tube T on one side. The B-24 joint at B can be connected to a sintered glass crucible. A manometer having a vacuum stop cock I on its one limb is connected through its other limb to the sintered crucible at C. The apparatus can be evacuated through the vacuum stop cock II. The sintered glass crucible with mercury acted as a seal and liquid mixtures can be introduced through it with the help of a syringe. At the point of standard joints and stop cocks I and II cups are made which are filled with mercury to act as seals. The side tube
FIG. 3.3. Molar excess enthalpies $H^E$ of Benzene $^{(i)} +$ Carbon tetrachloride $^{(j)}$ at 298.15K.

- Literature value
- Present work

Mole fraction of benzene

$HE$
FIG. 3.7. STATIC VAPOUR PRESSURE APPARATUS

MERCURY SEAL

TO VACUUM

MERCURY SEALS

SINTERED GLASS CRUCIBLE

MERCURY SEAL

MERCURY SEAL

TO VACUUM

FLASK

B-24

MERCURY

MERCURY
T has a B-10 standard joint which ends in a cup filled with mercury to seal it from outside atmospheric pressure. The composition of the solution can be measured by taking the solution from the side tube T with the help of a syringe having a long tube at its end. The U-tube of manometer was filled with the appropriate amount of mercury.

**Experimental Procedure**

The apparatus was attached to a high vacuum pump (model - PRI, Hind High Vacuum Co. (P) Ltd., Bangalore). Stop cock II was first closed while stop cock I was opened slowly and then closed immediately when the mercury just passed through the stop cock I. The stop cock I was then closed and the apparatus was evacuated through the stop cock II. The process was repeated till with the stop cock I closed and stop cock II opened slowly mercury in the limb D touched the stop cock I and there was no air space between it and stop cock I. The apparatus was finally evacuated through stop cock II, and the difference in the level of mercury in the two limbs of the manometer was noted (zero correction). The liquid mixture was then introduced in the flask A through the mercury filled sintered glass crucible with the help of a syringe. The mixture was degassed by alternately heating and cooling followed by evacuation. After the degassing process, the apparatus except manometer was placed in a water thermostat controlled to within ± 0.01 K. The manometer was kept at a higher temperature in an air thermostat controlled to within ± 0.1 K to avoid condensation. The manometer reading were taken with a cathetometer which could read correctly to ±0.001 cm.
The vapour pressures thus measured were corrected to 0° and standard gravity. The composition of the liquid mixtures at equilibrium was determined from their refractive index measurements.

**Determination of liquid compositions**

The composition of the liquid mixture was determined by measuring its refractive index at the temperature at which vapour pressures were measured. The dependence of the refractive index at that temperature was studied for a series of solutions of known compositions, and results were expressed by the relation:

\[ n_t^{(\text{mix})} = a' + b'x_1 + c'x_1^2 \]  \hspace{1cm} (13)

where \( a' \), \( b' \) and \( c' \) are constants and \( x_1 \) is the mole fraction of the component in the \((i+j)\) binary mixture. Constants \( a' \), \( b' \) and \( c' \) could be calculated by least square method from the refractive index data of known compositions. This was then used inversely to obtain the composition of the liquid from the values of refractive indices (measured with an Abbe's refractometer), maintained at the temperature of experiment. Measurements were taken out in triplicate and the mean error of \( \pm 0.1 \) per cent for composition was evaluated.

**Nuclear Magnetic Resonance studies**

Samples for NMR studies were prepared by mixing aniline with pyridine or \( \gamma \)-picoline and 1,2-dichloroethane with \( \alpha \)-picoline, by weight, in the NMR tubes followed by dilution with a fixed quantity of an inert solvent, cyclohexane.
Inert solvent does not effect the nature of binary interactions of aniline or 1,2-dichloroethane with pyridine and picoline). Immediately after preparation a fixed quantity of tetramethysilane (TMS), (used as internal reference), was added to each tube and the chemical shift of the NH$_2$ protons of aniline or the protons of 1,2-dichloroethane relative to TMS was detected on a varian 90 MHz spectrometer using sideband method$^{15}$. The chemical shifts were averaged over three determinations and were reproducible to within ±0.5 Hz.
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