CHAPTER III
MATERIAL AND METHOD
CHAPTER III

Purification of Organic Compounds & Experimental Methods

Benzene

Benzene (E. Merck, Analytical grade) was shaken repeatedly with about 15% of its volume of concentrated sulphuric acid in a stoppered separating funnel, until the acid layer was colourless or very pale yellow on standing. After each shaking, lasting a few minutes, the mixture was allowed to settle and the lower layer of acid was drawn off. The benzene layer was shaken with water many times in order to remove all the acid, dried over anhydrous calcium chloride and then distilled. It was then stored over sodium wire.

Toluene

Toluene (E. Merck, Analytical grade) was purified in the same manner as that for benzene. However it was subjected to occasional cooling, keeping the temperature below 30°C.

Xylenes

o- (E. Merck), m- (Fluka AG), p-xylenes (Thomas Baker & Co., London, Analytical grade) were purified in the same way as that for toluene or benzene.

Acetone

Acetone (E. Merck, Analar Grade) was refluxed with
successive small quantities of potassium permanganate until the violet colour persisted. It was then dried over anhydrous calcium sulphate, filtered and then fractionally distilled.

**Dioxane**

Dioxane (E. Merck, Analar grade) was refluxed with sodium metal as suggested by Rastogi and McGlashan, and then fractionally distilled.

**Bromoform**

Bromoform (E. Merck, Analay grade) was shaken vigorously with 10% sodium bicarbonate solution and then dried with calcium chloride. It was left overnight and then fractionally distilled.

**o-Chlorotoluene**

o-Chlorotoluene (J.T. Baker Chemical Co. U.S.A.) was purified by fractional distillation.

The purity of the purified compounds was checked by measuring their densities at 298.15 ± 0.01 K. These agreed well with the values reported in literature²⁻¹⁴, as is evident from Table 1. For o-chlorotoluene and bromoform, the density at 298.15 K was evaluated from the density data reported at different temperatures in the literature¹¹,¹².
<table>
<thead>
<tr>
<th>Compound</th>
<th>Density in gm cm$^{-3}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental value</td>
<td>Lit. value</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.87368</td>
<td>0.87363$^8$ Nyvlt et al. (1961)</td>
</tr>
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<td>Toluene</td>
<td>0.86226</td>
<td>0.86232$^9$ Kyle et al. (1958)</td>
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<tr>
<td>o-Xylene</td>
<td>0.87600</td>
<td>0.87596$^{10}$ Forziati et al. (1949)</td>
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<td>m-Xylene</td>
<td>0.85985</td>
<td>0.85990$^{10}$ Forziati et al. (1949)</td>
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<tr>
<td>p-Xylene</td>
<td>0.85673</td>
<td>0.85669$^{10}$ Forziati et al. (1949)</td>
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<td>o-Chlorotoluene</td>
<td>1.076$^{+4}$</td>
<td>1.076$^{+0}$ Timmermans (1950)</td>
</tr>
<tr>
<td>Bromoform</td>
<td>2.87755</td>
<td>2.87751$^{12}$ Timmermans (1950)</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.7845</td>
<td>0.7846$^{13}$ Albright (1937)</td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td>1.0279</td>
<td>1.0280$^{14}$ Teague and Felsing (1943)</td>
</tr>
</tbody>
</table>

Measurements of molar excess volumes

Molar excess volumes for binary as well as ternary mixtures of non-electrolytes were measured in a two limbed and three limbed specially designed dilatometer$^{15}$ respectively.

Description of the dilatometer

The dilatometers used in the present work (as shown in Fig 3.1) consist of two limbs (in case of binary mixtures)
Fig. 3.1. Dilatometer for molar excess volumes
and three limbs (in case of ternary mixtures) having vacuum tested B-7 standard joints at their ends. The limbs are interconnected through a small bent tubing. A thin uniform bored capillary having a reference mark, R, is fused to the side of compartment A as shown in Fig. (3.1).

Experimental procedure for $V_{ij}^E$

A column of mercury was placed in the dilatometer and weighed. One of the degassed liquids say (i) was added in the bulb B or C with the help of a hypodermic syringe (having a long 9 inches needle at its end). The bulb was then closed with its stopper in such a way so that no air bubbles were entrapped in it. The dilatometer was again weighed. The second degassed liquid (j) was then added to the bulb A and the stopper was replaced keeping the liquid level in the capillary at a suitable position. The dilatometer was then placed in a water thermostat controlled to $\pm 0.01$ K or better by a mercury-in-toluene regulator. The reference mark and the liquid level in the capillary were noted with the help of a cathetometer (M/S Osaw, Ambala) which could read to $\pm 0.001$ cm.

After the thermal equilibrium had been attained, the contents of the dilatometer were mixed by tilting it gently sideways several times. In order to ensure that the liquid in the capillary had the same composition as that of the bulk solution on mixing, the dilatometer was placed in a cold bath so that minimum liquid was there in the capillary. The dilatometer
was again placed in the thermostat and this procedure was repeated three or four times. The reference mark and the level of the liquid in the capillary were again noted after thermal equilibrium. The dilatometer was then taken out of the thermostat, dried completely, and weighed, to determine the weight of the second liquid (j).

The molar excess volumes for the ternary (i+j+k) mixtures were determined exactly in the same way as that described for the (i+j) mixture except that the three components i, j and k were now taken in the three bulbs A, B & C.

Molar excess volumes, $V_{ij}^E$, for binary (i+j) mixtures were then calculated from the expression

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

... (1)

where $\pi r^2$ is the area of the capillary and $\Delta h$ is the change in the liquid level in the capillary after mixing, $r$ is the radius of capillary, and $(n_i + n_j)$ are the total number of moles of (i+j) mixture. The dilatometer's capillary was calibrated from the weight of a length of mercury column in it. The length of the mercury column in the capillary at various positions was read by a travelling microscope that could read to ± 0.001 cm. The density of mercury was taken from literature at the room temperature of that day. From the weight of the mercury column of length $l$, the $\pi r^2$ of the capillary
was evaluated from

$$\pi r^2 = \frac{W_{Hg}}{\rho_{Hg} \times l_{Hg}}$$

where $W_{Hg}$ = mass of an average length of mercury

$$\rho_{Hg} = \text{density of mercury}$$

Similarly for a ternary $(i + j + k)$ mixture, $V_{ijk}^E$ can be evaluated from

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

where

$$\Delta h = \text{change in the liquid level in the capillary on mixing and}$$

$(n_i + n_j + n_k)$ = total no. of moles of the $(i+j+k)$ mixture.

**Sources of error**

The $V^E$ values so obtained are subject to errors from the following sources.

1. **Instrumental error**

   Equation (1) can be rewritten as

   $$V_{ijk}^E = (W/\rho l) \Delta h / (n_i + n_j) \quad \ldots \quad (3)$$

   where $W$ is the weight of mercury having length equal to 1 cm and $\rho$ is its density. The error in $V^E$ could then be due to errors in the measurements of $W$, $\rho$, $l$, $h$ and $(n_i + n_j)$. 

From equation (3) it follows that

$$\frac{dV_{ij}^E}{V_{ij}^E} = \left[ \frac{dw}{w} - (d\rho) - (dl) + (\frac{d\Delta h}{\Delta h}) - \left( \frac{d(n_i + n_j)}{(n_i + n_j)} \right) \right] \times 100 \quad \ldots (4)$$

Equation (4) then gives the percentage error in the $V_i^E$ values and can be determined if the uncertainties in the $w, \rho, l, \Delta h$ and $(n_i + n_j)$ are known. For a typical benzene(i) + o-chlorotoluene(j) mixture at $x_i = 0.5242$ at 298.15 K the uncertainties in $w, l, \rho, \Delta h$ etc. are

- $dw = 0.0001$ gm
- $d\rho = 0.0005$ gm cm$^{-3}$
- $dl = 0.001$ cm
- $d(\Delta h) = 0.001$ cm
- $d(n_i + n_j) = 0.0001$ mol

\[ w = 0.2784 \text{ gm} \]
\[ \rho = 13.53400 \text{ gm cm}^{-1} \]
\[ l = 10.550 \text{ cm} \]
\[ \Delta h = 9.948 \text{ cm} \]
\[ (n_i + n_j) = 0.0887 \text{ mol} \]
\[ \Delta T = \pm 0.01 \text{ K} \]

so that total error in the measured $V_{ij}^E$ values of the (i+j) mixture comes out to be $\pm 0.5\%$.

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

$$V_{ijk}^E = (w/\rho l)\Delta h/ (n_i + n_j + n_k) \quad \ldots (5)$$
IIS gives the percentage error in the measured molar excess volumes for the ternary system and can be readily determined if the uncertainties in the values of \( w, l, \Delta h \) and \( n_1 + n_j + n_k \) for an \((i + j + k)\) mixture are known. For a typical benzene\((i) + toluene(j) + o\)-chlorotoluene\((k)\) at \( x_i = 0.4249 \) and \( x_j = 0.4188 \) (\( x_i, x_j \) are the mole fractions of components \( i, j \)) at 308.15 K these values are given below.

\[
\begin{align*}
\text{d}w &= 0.0001 \text{ gm} \\
\text{d}l &= 0.001 \text{ cm} \\
\text{d}l &= 0.00005 \text{ gm cm}^{-1} \\
\text{d}(\Delta h) &= 0.001 \text{ cm} \\
\text{d}(n_1 + n_j + n_k) &= 0.0001 \text{ mol} \\
\end{align*}
\]

\( \rho = 13.53400 \text{ gms cm}^{-1} \)

\( \Delta h = 2.884 \text{ cm} \)

\( \frac{\text{d}(n_1 + n_j + n_k)}{n_1 + n_j + n_k} = 0.0191 \text{ mol} \)

\( \Delta T = \pm 0.01 \text{ k} \).

So that the total error in the measured \( V_{ijk}^E \) of the \((i+j+k)\) mixture due to all these uncertainties, comes out to be \( \pm 0.52\% \).

**Errors due to evaporation**

Molar excess volumes measured in the present investigation are also subject to errors due to the evaporation of liquids from the capillary. However since the measured \( V_{ij}^E \)
values for benzene (i) + toluene (j) mixture at 298.15 K deviate as much as 0.0005 cm$^3$ mol$^{-1}$ (at the worst) from the values reported for this mixture, the errors in $V_{ij}^E$ values due to this factor is not a serious one.

Errors due to change in the area of cross section of capillary

Change in temperature can also change the internal area of cross section of capillary at a temperature far away from the calibrated temperature. An analysis of the measured $V_{ij}^E$ values for benzene (j) + cyclohexane (l) mixtures, at 298.15 K has shown that the errors due to this cause are also negligible.

The reliability of the present dilatometers were checked by measuring molar excess volumes for benzene (j) + cyclohexane (l) mixture at 298.15 K and these agreed well with the best values reported for this mixture in the literature (see Fig. 3.2).

Measurement of molar excess enthalpy

The molar excess enthalpy of the present mixtures were determined using a flow micro-calorimeter (LKB, Broma, Sweden).

General description of the apparatus

The arrangement of the apparatus is shown in Fig. (3.3). A metal block heat sink 'a', contains a centrally located heat exchange unit, 'b', surrounded by calorimetric unit c, in a twin arrangement. The calorimetric units consist of flow reaction cells surrounded by surface thermopiles which are in contact
FIG. 3.2. Molar excess volumes $V^E$ of Cyclohexane (i) + Benzene (j) at 298.15 K.

- Literature value
- Present work
with primary heat sinks. The heat sink is thermally insulated and immersed in a thermostated water bath. The calorimetric liquids are pumped through the heat exchange unit to one of the reaction cells and from there to a receiver outside the calorimetric system.

The voltage signal recorded at an experiment is the differential signal from the two thermopiles and external thermal disturbances are therefore largely expected to cancel. Liquid flows only through one cell during an experiment and a correction is applied for zero effects arising from liquid flow.

**Calorimetric principle**

The two calorimetric liquids are brought together in a mixing zone of the flow cell. A constant flow rate gives rise to a constant heat effect in the calorimetric cell. If this heat effect is allowed to continue long enough steady state conditions will be established, i.e. heat generated in the cell will per unit time be equal to the heat transported out from the cell. The steady state conditions is thus the most accurate method of operating the present calorimeter and this is the principle which is discussed here.

A major part of the heat effect generated in the cell \( W \) at steady state is the transport of heat from the cell by conduction through the surrounding thermopile \( W_t \), and to a minor extent to the heat lost through the air gap between parts of
flow cell surface not in contact with the thermopile. A small fraction of the total heat effect generated will also leave the cell by the liquid flow.

It may be expected that for a given calorimeter and for stated values for flow rate, reaction rate and physical properties of the calorimetric liquid, the fraction $W_t/W$, will be constant i.e.

$$W = \alpha \cdot W_t$$  \hfill (7)

The transversal temperature gradient at various parts of the thermopile is expected to be proportional both to the heat flow and to the voltage generated. Integration over the total thermopile area then leads to the expression

$$W_t = \Theta \cdot V$$  \hfill (8)

where $\Theta$ is a constant and $V$ is the thermopile voltage. Combination of (7) and (8) yields

$$W = \alpha \cdot \Theta \cdot V = \xi \cdot V$$  \hfill (9)

Again a small fraction of the heat effect generated in the cell is a consequence of the flow of liquid through the cell, such as heat of friction etc. The contribution to the thermopile signal from this latter heat effect may be determined at separate zero experiments. If this thermopile value is taken as the reference point for the thermopile voltage at the main experiment then

$$W_p = \xi \cdot V_p$$  \hfill (10)
where $W_p$ is the heat effect connected with the process occurring in the flow cell and $V_p$ is the displacement of the thermopile voltage value from the determined base line. The constant $\mathcal{E}$ is determined by electrical calibration.

**Zero effects**

Heat effects generated by a process under steady state conditions is calculated through equation (10), i.e. $W_p = \mathcal{E} \cdot V_p$. Here $V_p$ is the displacement of the thermopile signal from a certain voltage base line to the recorded steady state value. The base line value varies slightly with the experimental conditions. The zero effect may be expressed in terms of a heat effect, $W'$

$$W' = \mathcal{E} (V' - V_0) \quad \ldots (11)$$

where $V_0$ is the thermopile voltage under apparent equilibrium conditions for the calorimeter and when the flow rate was zero. $V'$ is the thermopile voltage (the base line value) at the specified liquid flow. $V_0$ is usually not zero even after a very long equilibration time for the calorimeter.

**Zero effects at different flow rates:** At different flow rates the zero effect varies i.e. becomes positive or negative and $W'$ is quite sensitive to variations in the flow rate.

**Variation in zero effect with the viscosity of the calorimetric liquid**

Variation in zero effect takes place when, at a constant
flow rate, the calorimetric liquid changes viscosity.

Experimental procedure for $H^E$ for (i+j) & (i+j+k) mixtures

Molar excess enthalpies $H^E_{ij}$ were determined by an LKB flow microcalorimeter (LKB-2107, M/S LKB Broma, Sweden) in the manner described by Monk and Wadso. According to the specification of instrument the temperature can be set with a precision of 0.1 K and its stability is 0.02 K/24 h. Two identical Braun Perfuser Pumps (B. Braun, Melsungen AG, W. Germany) and gas tight Hamilton syringes were employed to pump liquid through the calorimeter. By the use of 10, 20 and 50 cm$^3$ syringes and the 10 speed gear boxes of the perfuser pumps, different mixing ratios were achieved. The flow rates were determined by pumping distilled water through the calorimeter, and weighing the amounts collected in a specific time interval. For each typical $H^E$ measurement, different calibration constants were determined according to the flow rate, the amplification needed, and the composition of the mixture.

Molar excess enthalpies for (i+j) mixture per mol were then evaluated from

$$H^E_{ij} = C^2 R \frac{\Delta h_1}{\Delta h_2} / (n_i + n_j)$$

... (12)

where $C$ is the current in amperes, $R$ is the resistance of the calorimeter heater in ohms, $\Delta h_1$ is the factor used to determine the amount of heat during compensation, $\Delta h_2$
and $\Delta h_2$ have the same significance as described by Adcock and McGlashan. The reliability of the instrument was checked by measuring the $H_{ij}^E$ values for benzene(i) + carbon tetrachloride(j) mixtures at 298.15 K and these agreed, to within the experimental limits, with the corresponding experimental values.

Molar excess enthalpies for ternary (i+j+k) mixtures were determined in the same way as in the case of (i+j) mixtures, except that in one of the syringes a mixture of known composition (by weight) of (i+j) or (j+k) or (i+k) was taken and in the other syringe the third pure component was allowed to run through. The basic idea in calculating the $H_{ijk}^E$ is that $H_{ijk}^E$ is the sum total of the heat evolved or absorbed when a ternary mixture (i+j+k) is running through the calorimeter plus the heat evolved or absorbed in preparing (j+k) mixture of known composition. Molar excess enthalpies for the (i+j+k) mixtures were then calculated from the relation

$$H_{ijk}^E(x_i, x_j) = \frac{(Q_{i+j+k} + Q_{j+k})}{(n_i + n_j + n_k)} \ldots (13)$$

where $Q_{i+j+k}$ is the heat evolved in Jouls when in one syringe pure liquid (i) is allowed to run while, in the other, mixture of (j+k) of known composition is taken. $Q_{j+k}$ is the heat evolved in the binary system of (j-k) of known composition. Further since

$$Q_{j+k} = H_{j+k}^E \times n_{j+k}$$

where $n_{j+k}$ are the total number of moles of binary system (j+k) in the ternary mixture at the desired flow rate,
Fig. 3.4 Molar excess enthalpies $H_E$ of Benzene (i) + carbon tetrachloride (j) at 298.15 K

- Literature value
- Present work
equation (8) takes the form

\[ H_{i+j+k}^{E} = H_{j+k}^{E} + Q_{i+j+k} / (n_i + n_j + n_k) \]  ... (14)

Further the number of moles and the mole fraction of the various components in the ternary mixture were calculated from the following relations

\[ n_i = \frac{f_{r_1}}{V_i} \]  ... (15)

\[ n_j = x_j \cdot f_{r_2} \cdot \frac{1}{\left[ V_{E,j+k} \cdot (x_j V_{j} + x_k V_{k}) \right]} \]  ... (16)

\[ n_k = x_k \cdot f_{r_2} \cdot \frac{1}{\left[ V_{E,j+k} \cdot (x_j V_{j} + x_k V_{k}) \right]} \]  ... (17)

where \( V_{E,j+k} \) is excess volume at the known composition of \( j \) in a \((j+k)\) mixture, while \( V_i \) etc. is the molar volume of \( i \) etc. entities and \( x_j \) and \( x_k \) are the mole fraction of \( j \) and \( k \) in the \((j+k)\) mixture, respectively. \( f_{r_1} \) is the flow rate of the liquid running in the syringe No. 1 and \( f_{r_2} \) is the flow rate of liquid running in syringe No. 2.

**Sources of error in \( H^E \) determination**

Molar excess enthalpies measured in the present set up are subjected to the following instrumental errors.

**Instrumental Errors**

These errors can be determined easily, as e.g. for a binary \((i+j)\) mixtures we have
The percentage error in $H_{ij}^E$ was calculated by considering the errors in the individual quantities $C$, $R$, $\Delta h_1$, $\Delta h_2$ and $(n_1 \cdot n_j)$.

For a binary $(i+j)$ mixture it follows from equation (12) that

$$\frac{dH_{ij}^E}{H_{ij}^E} = \left[\frac{dC}{C} + \frac{dC}{C} + \frac{dR}{R} + \frac{d(\Delta h_1)}{\Delta h_1} - \frac{d(\Delta h_2)}{\Delta h_2} - \frac{d(n_1 \cdot n_j)}{n_1 \cdot n_j}\right] \times 100$$

For o-xylene $(i)$ + o-chlorotoluene $(j)$ system at 298.15 K at mole fractions $x_i = 0.1669$; $x_j = 0.8331$, we have

$$C = 0.009 \text{ ma} \quad \Delta C = 0.00005 \text{ ma}$$

$$R = 49.3 \text{ ohm} \quad \Delta R = 0.1 \text{ ohm}$$

$$\Delta h_1 = 17 \text{ mm} \quad \Delta(\Delta h_1) = 1.0 \text{ mm}$$

$$\Delta h_2 = 27 \text{ mm} \quad \Delta(\Delta h_2) = 1.0 \text{ mm}$$

$n_1 \cdot n_j = 8.425 \times 10^{-6} \text{ moles per sec.} \quad d(n_1 \cdot n_j) = 0.01 \times 10^{-6} \text{ moles per sec.}$

so that error in $H_{ij}^E$ due to all these uncertainties is about 1%.

Similarly for a ternary system of benzene $(i)$ + toluene $(j)$ + o-chlorotoluene $(k)$, since $H_{ijk}^E$ is given by

$$H_{ijk}^E = C^2 R \frac{\Delta h_1}{\Delta h_2} / (n_1 \cdot n_j \cdot n_k),$$

it follows from this equation that
\[
\frac{d H_{ijk}^E}{H_{ijk}^E} = \left[ \frac{dC}{C} + \frac{dC}{C} + \frac{dR}{R} + \frac{d(\Delta h_1)}{\Delta h_1} - \frac{d(\Delta h_2)}{\Delta h_2} \right] \times 100
- \frac{d(n_i n_j n_k)}{n_i n_j n_k}
\]

For a ternary system of benzene (i) + toluene (j) + o-chlorotoluene (k) system at \( x_i = 0.2939, x_j = 0.1416 \) at 298.15 K

\[
\begin{align*}
C &= 0.009 \text{ ma} \\
R &= 49.8 \text{ ohms} \\
\Delta h_1 &= 18 \text{ mm} \\
\Delta h_2 &= 17 \text{ mm}
\end{align*}
\]

\((n_i n_j n_k) = 7.80 \times 10^{-6} \text{ moles per sec}, \quad d(n_i n_j n_k) = 0.01 \times 10^{-6} \text{ moles per sec.}\)

So that error in \(H_{ijk}^E\) due to all these uncertainties is about 1.0%.

Molar Excess Gibbs Free Energy

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

Description of apparatus

The apparatus is shown in Fig. (3.5). It consists of a flask A having a 3-24 standard joint at its neck at B and a
FIG. 3.5. STATIC VAPOUR PRESSURE APPARATUS.
side tube T at 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 glass crucible at C. The apparatus can be evacuated through a 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 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 (Hind Vacuum Co. (P) Ltd. Bangalore, Model - VS-4). The 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 stop cock II. The process of evacuation through stop cock I and II was repeated till there is no air bubbles in the two limbs so that level of the mercury in the two limbs is stationary. The difference in the level of mercury in the two limbs was then 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 with long neck. The mixture was then degassed by alternative heating and cooling followed by evacuation. After the degassing process, the apparatus was kept in the water thermostat controlled to within ± 0.01 K. After about half an hour when the solution had attained the thermal equilibrium, the manometer readings were taken with a cathetometer (M/S OSAW, Ambala) which could read correctly to ± 0.001 cm. The vapour pressure, thus measured, were next corrected to 0° and standard gravity. The reliability of the instrument was checked by measuring the vapour pressure of our pure organic compounds and comparing them with the corresponding literature values.

Table 2. Comparison of the vapour pressure data at 303.15 K of the various compounds with their corresponding literature values.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Vapour pressure in mm of Hg</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exptl.</td>
<td>Lit. value</td>
</tr>
<tr>
<td>S Benzene</td>
<td>143.4</td>
<td>143.5</td>
</tr>
<tr>
<td>Toluene</td>
<td>46.3</td>
<td>46.8</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>11.7</td>
<td>11.8</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>13.2</td>
<td>13.2</td>
</tr>
<tr>
<td>o-Chlorotoluene</td>
<td>6.4</td>
<td>6.4</td>
</tr>
</tbody>
</table>
Examination of the liquid compositions

For this purpose, the dependence of the refractive index at that temperature was studied for a series of solutions of known composition and the results were expressed by the relation

\[ n_{mix}^t = a^1 + b^1 x_i + c^1 x_i^2 \]

where \( a^1, b^1 \) and \( c^1 \) are constants and \( x_i \) is the mole fraction of \( i \) component in the \((i+j)\) binary mixture. Constants \( a^1, b^1 \) and \( c^1 \) could be calculated by least square method from the refractive index data of known composition. This was then used inversely to obtain 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 in triplicate. The refractometer readings were reproducible to \( \pm 0.0002 \) and the measured compositions are accurate to \( 0.1 \) mole percent. The final composition was, however, determined interferometrically using a Carl-Zeiss interferometer.

U.V. and N.M.r studies

Samples for U.V. absorption studies were prepared by mixing (i) \( 10^{-4} \) M solutions of bromoform and 1,4-dioxane and (ii) \( 10^{-4} \) M solutions of bromoform and acetone in analytical grade cyclohexane and their spectra (in the UV region) were recorded on a spectronic 2000 spectrophotometer (Bausch and Lomb) according to Job's method of continuous variation.28
Samples for NMR studies were prepared by mixing (by weight)

(a) (i) bromoform with 1,4-dioxane

(ii) bromoform with acetone

in NMR tubes followed by dilution with a fixed quantity of an inert solvent (cyclohexane) and immediately after preparation of samples, tetramethylsilane (as an internal indicator) was added. NMR spectra of these samples were taken on a Perkin Elmer R-32 (90 MHz) spectrometer using side band method.29

(b) we next prepared equimolar benzene + o-chlorotoluene mixture, by weight in an NMR tube, diluted with a known volume of cyclohexane (spectroscopic grade) and TMS was added immediately after preparation of the mixture. NMR spectra of this equimolar mixture was recorded on a Varian 90 MHz spectrometer. Using this solution as solvent, we next recorded NMR spectra of benzene (i) + o-xylene (j) + o-chlorotoluene (k) mixtures.
References


2. Ref. 1, p. 267.

3. Ref. 1, p. 698.


7. Ref. 1, p. 699.


12. Ref. 11, p. 221.


20. Ref. 19, p. 1848.


