CHAPTER 4

EXCESS ENTHALPY AND NMR SPECTROSCOPIC STUDIES
The excess enthalpies, $H^E$, for binary mixtures of non-electrolytes provide reliable information regarding the nature of interactions occurring between the components of these mixtures. Thus, while high exothermic enthalpy of mixing values at low temperatures have been interpreted by McGlashan, Marcom and other workers\textsuperscript{1-3} to indicate complexation between the unlike molecules of the mixtures, endothermic enthalpies of mixing have been interpreted generally in terms of breakage of local bonds in the pure components.

Excess enthalpies are usually determined by two methods:

1) From the temperature dependence of the excess free energy, derived from vapour pressure measurements at a series of temperatures.

2) From direct calorimetric measurements from the mixing process.

It has been observed\textsuperscript{4-5} that reliable values of excess enthalpies can not be obtained from excess free energy of mixing. The uncertainty in these vapour pressure derived $H^E$ values arises, firstly, due to the small temperature range which forces one to compute small difference between large numbers and, secondly, the necessity of making corrections for gas imperfections which are much
larger (because of the high vapour pressure at high 
temperature). The values of $H^E$ thus obtained are often 
inaccurate and cannot be depended upon. The direct 
calorimetric method (either an adiabatic or an isothermal) 
however gives satisfactory results. In the adiabatic mode, 
the mixing vessel is kept in thermal isolation. If $H^E$ is 
positive, a lowering of temperature takes place on adiabatic 
mixing, and the fall in temperature is nullified by simul-
taneous or a subsequent supply of heat. If the heat is 
supplied simultaneously, mixing is done under conditions 
which are more or less isothermal, and the correction factor 
for the exchange of heat with the surroundings becomes very 
small. If $H^E$ is negative, there is a rise in the mixtures 
temperature and this rise is measured.

McGlashan has made an extensive review of the 
subject. A brief account of the developments in calori-
meter designing is given below.

Hirobe was the first to carry out $H^E$ measurements 
for about fifty-one pairs of liquids. In his experimental 
set up, the two components were separated by a thread of 
mercury in a V shaped glass mixing vessel. However, 
these liquids were not completely out of contact with 
their vapours and mixing was done by inverting the 
mixing vessel. A refined version of this calorimeter was 
used by Scatchard to make $H^E$ measurements. He mounted 
the mixing cell on a wheel and suspended it in a dewar 
flask. The calorimeter was rotated at an angle of 
about 270° in opposite directions at a constant rate
to mix the components. This rotation continued during the experiment. The calorimeter used by Hirobe has been modified by several workers. Cheesman et al. on the other hand, used a calorimeter which consisted of two copper chambers and in which the two components were separated by a thin tin foil diaphragm. This diaphragm was pierced by a point steel breaker manipulated by an external magnet to mix the two components.

van der Waals and Hermans used a metal calorimeter in which the components were separated by means of a ground-in-stopper. However, in the calorimeters described by Kortum et al., Ruiter and Brown et al., one of the components was confined in a glass ampule immersed in the second liquid, and the ampule was broken with a stirrer to mix the components.

The main shortcoming in all these calorimeters is that they had vapour space in contact with the liquid which causes the evaporation of the liquids. Although some of the calorimeters described above have negligible vapour space, detectable error was found in the measurements of $H^E$. Adcock and McGlashan designed a twin calorimeter in which the vapour space above the liquid was eliminated by confining the liquids under mercury. This calorimeter has further been improved by Larkin and McGlashan and various other workers. Van Ness, however, designed a continuous dilution calorimeter for $H^E$ measurements. This design allowed measurements of integral heats of mixing to be made to mole fractions as low as 0.001 and at the same time, provided means for the direct determination of partial molar heats of mixing with an accuracy of ±1%.
An improved version of this calorimeter has been used by Stokes et al.\textsuperscript{26} and Klappa et al.\textsuperscript{27-28} An isothermal dilution calorimeter for positive enthalpies has been described by Gracia\textsuperscript{29} this calorimeter has the advantage that mercury is not necessary. Flow micro calorimeters are fast gaining importance and have been used and improved by several workers.\textsuperscript{30-38} Krishnan et al.\textsuperscript{39} have used micro-flow calorimeter to study the self association of compounds due to hydrogen bonding. The calorimeter designed by Nigam et al.\textsuperscript{40} was used in carrying out the present $H^E$ measurements.

**Experimental**

The calorimeter is shown in figure 4-I. It consists of a double walled glass mixing vessel made up of two compartments A and B having B-7 and B-12 standard joints at their ends. These were inter-connected through a bent tubing C. A side tube with a capillary D and bulb E was fused to the bent tubing C as shown in the figure. The other jacket of the calorimeter was evacuated through the outlet x. A glass tube of approximately 2.5 cm length was fused with the B-12 cone. The calorimeter heater (resistance $14.062 \, \Omega$) was made up of insulated constantan wire wound round the glass tube fused with the B-12 joint. A thermistor (resistance $\approx 200 \, \Omega$) was inserted through this glass tube to record the change in temperature. This thermistor was enclosed in a very thin steel capsule, which was fixed to the open end of the glass tube with araldite. The gap between
the steel capsule and the thermistor was filled with mercury in order to make it a good conductor of heat. The two liquids in compartments A and B were separated by mercury. A part of the capillary was filled with mercury to prevent the direct contact of the liquids with the atmosphere. Mixing was done by slightly side tilting the apparatus (calorimeter) without letting the liquids to come near the capillary D. The apparatus was mounted on an automatic mixing device (regulated speed) which tilted the calorimeter by about 45° on either sides of the vertical. The speed of the mixing device was so adjusted that only 1/2 to 1/4 were given to the calorimeter in one minute. This rate ensured complete and smooth mixing of the components. The capillary D and the bulb E provide an air space in D, which inspite of remaining alien to the liquid, ensures pressure constancy in the calorimeter when there is a change of volume during the mixing.

Electrical Circuits

The set up consists of two electrical circuits:

1) Heating Circuit and
2) The Thermistor Circuit.

The heating circuit is shown in figure 4-II. It consists of a 6 volt battery B connected to a milliammeter A, and one ohm standard 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
(shown in figure 4-III) consisting of two arms with adjustable resistances \( P \) and \( Q \). \( R \) and \( S \) are the thermistor (\( \approx 200 \Omega \)) and a resistance of a value of the same order. A potentiometric recorder \( P \) (Toshniwal Type 1002) was used instead of the galvanometer to record the offset of the null point. The bridge was supplied with current from a stabilized power supply.

**Experimental Procedure**

An appropriate amount of mercury was placed in the calorimeter and it was weighed. One of the degassed liquids was added to the compartment \( A \) and stoppered tightly ensuring that no air bubble was entrapped. The calorimeter was reweighed. The second degassed liquid was then added to compartment \( B \) and the stopper replaced so that the mercury level in capillary \( D \) was at a suitable position. The calorimeter was again weighed and then immersed in a thermostatic bath controlled to \( \pm 0.01K \) by means of toluene regulator. The contents were allowed to attain thermal equilibrium by keeping the calorimeter in the thermostatic bath for about two hours. The potentiometric recorder
was then switched on and the attainment of thermal equilibrium
was indicated by the appearance of a stable base line. The
outer jacket was then evacuated and the liquids were mixed
(after about half an hour) by tilting the calorimeter side­
ways with the help of the automatic shaker. Current was passed
through the calorimeter heater for compensation (in case of
endothermic reactions) and the time of passage was noted with
the help of an electronic counter timer (Systronics Type 701)
capable of reading correct to ± 0.0001 sec. When the slope
of the peak attained a constant value, current was again
passed for calibrating purposes 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:

\[ H^E = (C^2R_t - C^2R_{t_2} \frac{\Delta h_1}{\Delta h_2})/(n_1 + n_2) \]  \(1.1\)

where \(C\) is the current in amperes, \(R\) is the heater resistance
in ohms, \(t_1\) is the time for which the current was passed
for compensation and \(t_2\), 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 compensa­
tion. \(\Delta h_1\) and \(\Delta h_2\) have the same significance as described
by Adcock and McGlashan.\(^9\) In case of exothermic reactions,
the value of \(t_1\) becomes zero and \(H^E\) is then given as

\[ H^E = -C^2R_{t_2} \frac{\Delta h_1}{\Delta h_2} / (n_1 + n_2) \]  \(1.2\)
Sources of Errors

Excess enthalpy measurements are subjected to the following errors:

(1) **Instrumental Errors**

The instrumental error can be easily estimated as shown below.

We have \( H^E = \frac{C^2 R t_1 + C^2 R t_2 \Delta h_1 / \Delta h_2}{(n_1 + n_2)} \) ...(4.3)

If we put \( C^2 R t_1 / (n_1 + n_2) = A \) ...(4.4)

and \( C^2 R t_2 \Delta h_1 / \Delta h_2 (n_1 + n_2) = B \) ...(4.5)

the percentage error in \( H^E \) can be estimated by knowing the percentage errors in \( A \) and \( B \). The percentage errors in \( A \) and \( B \), in turn, can be estimated by the knowledge of possible errors in measurements of the quantities \( C, R, t_1, t_2, \Delta h_1, \Delta h_2 \) and \( (n_1 + n_2) \). For a typical run for a 1,2-dichloroethane + benzene mixture at \( x_1 = 0.4906 \).

\[
\frac{dA}{A} = 2 \frac{dc}{C} + \frac{dR}{R} + \frac{dt_1}{t_1} - \frac{d(n_1 + n_2)}{(n_1 + n_2)} \]  

\[
dc = 0.00001 \text{ ampere} \quad C = 0.14362 \text{ ampere} \]

\[
dR = 0.001 \text{ ohm} \quad R = 14.062 \text{ ohms} \]

\[
dt_1 = 0.0001 \text{ sec} \quad t_1 = 34.7125 \text{ secs} \]

\[
d(n_1 + n_2) = 0.0001 \text{ mol} \quad n_1 + n_2 = 0.0534 \text{ mol} \]

\[
\frac{dA}{A} = 0.00167
\]
Similarly,

\[ dB/B = 2dc/C + dR/R + dt_2/t_2 + d(\Delta h_1)/h_1 - d(\Delta h_2)/h_2 - \frac{d(n_1+n_2)}{(n_1+n_2)} \]  

(4.7)

\begin{align*}
dc &= 0.00001 \text{ ampere} \\
dR &= 0.001 \text{ ohm} \\
dt_2 &= 0.0001 \text{ sec} \\
d\Delta h_1 &= 0.05 \text{ cm} \\
d\Delta h_2 &= 0.05 \text{ cm} \\
d(n_1+n_2) &= 0.0001 \text{ mol} \\
dB/B &= 0.00112 \\
dt &= \pm 0.01K
\end{align*}

The total error is found to be \( \pm 1\% \)

(ii) Another source of error is the leakage of heat along with heater and thermistor wires due to the difference of temperature on mixing.

(iii) Errors are due to creep in if the temperature control and the stirring of the water in the thermostatic bath are inefficient.

The reliability of the calorimeter was checked by measuring molar excess enthalpy for benzene + cyclohexane mixtures at 298.15K. The data thus obtained are recorded in Table 4-1 and plotted in Figure 4-IV along with the data of Marsh et al. An excellent agreement of our \( H^E \) data with that of Marsh et al ensured the reliability of
<table>
<thead>
<tr>
<th>Temperature 298.15K</th>
<th>Temperature 298.15K</th>
<th>Temperature 308.15K</th>
<th>Temperature 318.15K</th>
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<td>$H^\text{E}$</td>
<td>Mole fraction of A</td>
<td>$H^\text{E}$</td>
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**TABLE 4-1**

Enthalpy of mixing data for various mixtures

Benzene (A) + cyclohexane (B)

1,2-Dichloroethane (A) + benzene (B)

contd...
1,2-Dichloroethane (A) + toluene (B)

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<td>Mole fraction of A</td>
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### 1,2-dichloroethane (A) + m-xylene (B)

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# 1,2-Dichloroethane (A) + aniline (B)

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<th>Mole fraction of A</th>
<th>$H^E$ (J mol(^{-1}))</th>
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Mole fraction of benzene.

Fig. 4-IV Excess enthalpy $H^e$ of benzene + cyclohexane
- (Experimental) and the corresponding
- values reported by Marsh. at

298.15 K
Melt fraction of lyS-dloteloroothwno
Vig* Mr Sxoo» onttuOpy H* of lt2-4*rtloro«fthan«
#,298.15*, a 3^8.15*, ©,J18.15K
b onion#

![Graph showing excess enthalpy $H^E$ of 1,2-dichloroethane + benzene](image)

**Fig. 4-V** Excess enthalpy $H^E$ of 1,2-dichloroethane + benzene

- $\bullet$, 298.15K
- $\triangle$, 308.15K
- $\bigcirc$, 318.15K
Fig. 1-VI  Excess enthalpy $H^E$ of 1,2-dichloroethane - volumes

$\circ 298.15K$, $\triangle 308.15K$, $\bullet 318.15K$
Fig. 6-VII Excess enthalpy $H^E$ of 1,2-dichloroethane + cyclohexane

- 298.15K
- 308.15K
- 318.15K
Mole fraction of 1,2-dichloroethane

Fig. 4-VIII Excess enthalpy $H^E$ of
1,2-dichloroethane + m-xylene

$\Theta$, 298.15K, $\Delta$, 308.15K, $\bigcirc$, 318.15K
Mole fraction of 1,2-dichloroethane

Fig. 4-IX Excess enthalpy \( H^E \) of 1,2-dichloroethane-p-xylene

\( \circ \) 298.15K, \( \Delta \) 308.15K, \( \odot \) 318.15K.
Mole fraction of 1,2-dichloroethane

Fig. 4-X Excess enthalpy $H^E$ of 1,2-dichloroethane + aniline

$\bullet$ 298.15K, $\bigcirc$ 308.15K.
The molar excess enthalpy values have been determined for the following mixtures at 298.15, 308.15 and 318.15 K:

1. 1,2-Dichloroethane + benzene
2. 1,2-Dichloroethane + toluene
3. 1,2-Dichloroethane + o-xylene
4. 1,2-Dichloroethane + m-xylene
5. 1,2-Dichloroethane + p-xylene
6. 1,2-Dichloroethane + aniline (298.15 and 308.15 K)

Results

The enthalpy of mixing data for the above mentioned mixtures at 298.15, 308.15 and 318.15 K are recorded in Table 4-1 and their plots are shown in figures 4-V to 4-X. The $H^E$ data were fitted to the equation

$$\frac{H^E}{x_1(1-x_1)}(J/mol^{-1}) = h_0 + h_1(2x_1 - 1) + h_2(2x_1 - 1)^2 \quad (4.8)$$

where $h_0$, $h_1$, and $h_2$ are disposable parameters and $x_1$ is the mole fraction of 1,2-dichloroethane. These parameters were evaluated by fitting the experimental value of $H^E/x_1(1-x_1)$ to equation (4.8) by the method of least squares and are recorded along with their deviation $\sigma(H^E)$ in Table 4-2.
Parameters of equation (4.8) along with the standard deviation $\sigma(H^E)$ of the molar excess enthalpy for the various mixtures at various temperatures.

<table>
<thead>
<tr>
<th>System</th>
<th>Temperature</th>
<th>$h_0$</th>
<th>$h_1$</th>
<th>$h_2$</th>
<th>$\sigma(H^E)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-Dichloroethane + benzene</td>
<td>298.15</td>
<td>171.9</td>
<td>71.1</td>
<td>31.2</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>308.15</td>
<td>215.7</td>
<td>91.7</td>
<td>61.8</td>
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<td></td>
<td>318.15</td>
<td>274.0</td>
<td>195.4</td>
<td>3.8</td>
<td>2.2</td>
</tr>
<tr>
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<td>298.15</td>
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<td>430.1</td>
<td>314.0</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>308.15</td>
<td>- 74.2</td>
<td>423.1</td>
<td>329.3</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>318.15</td>
<td>- 28.8</td>
<td>423.7</td>
<td>329.8</td>
<td>2.7</td>
</tr>
<tr>
<td>1,2-Dichloroethane + o-xylene</td>
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<td>614.3</td>
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<td>665.3</td>
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<td>720.0</td>
<td>339.8</td>
<td>2.1</td>
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<td>155.4</td>
<td>809.3</td>
<td>306.8</td>
<td>3.3</td>
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<td></td>
<td>318.15</td>
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<td>272.6</td>
<td>2.2</td>
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<tr>
<td>1,2-Dichloroethane + p-xylene</td>
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<td>722.7</td>
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<td></td>
<td>318.15</td>
<td>- 49.9</td>
<td>762.4</td>
<td>646.6</td>
<td>3.3</td>
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<tr>
<td>1,2-Dichloroethane + aniline</td>
<td>298.15</td>
<td>1104.3</td>
<td>85.1</td>
<td>154.1</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>308.15</td>
<td>1421.9</td>
<td>809.1</td>
<td>865.1</td>
<td>3.6</td>
</tr>
</tbody>
</table>
Discussion

The excess enthalpy of mixing data for all these mixtures at 298.15K are found to agree within ±2.5J with those reported by Mahl and Khurma. However, no $H^E$ data for 1,2-dichloroethane + aniline is available at any temperature in the literature with which to compare the present results.

$H^E$ data for 1,2-dichloroethane + benzene mixtures are found to be positive throughout the composition range and the temperature coefficient is also positive. In case of 1,2-dichloroethane + toluene, + o-xylene, + m-xylene and + p-xylene mixtures, there is a change in sign of $H^E$ values with the increase of 1,2-dichloroethane's mole fraction. The value of $H^E$ is initially negative at the lower mole fraction of 1,2-dichloroethane which attains a positive value as the mole fraction of 1,2-dichloroethane is increased. The $H^E$ data for 1,2-dichloroethane + aniline mixtures are positive over the complete 1,2-dichloroethane composition range and the temperature coefficient ($\partial H^E/\partial T$) is also positive for this system. The $H^E$ data for all these mixtures for an equimolar composition vary in the order

benzene $\rightarrow$ m-xylene $\rightarrow$ o-xylene $\rightarrow$ p-xylene $\rightarrow$ toluene.

At the simplest qualitative level, $H^E$ data can be explained if it is assumed that

1) electron donor-acceptor type interactions are occurring in these mixtures in which hydrocarbons...
ii) there is steric repulsion between the components of these binary mixtures.

According to Wilhelm et al., the rotation of both the components in 1,2-dichloroethane + benzene mixtures is hindered because of the charge transfer interaction between the π electrons of the benzene ring and the empty 3d levels of Cl-atoms in 1,2-dichloroethane. The introduction of a –CH₃ substituent in benzene, as in toluene, would render the π electron cloud in the aromatic ring of toluene to be more labile so that, compared to benzene, toluene should interact more strongly with 1,2-dichloroethane. This should imply a small positive value or H° for 1,2-dichloroethane + toluene mixture which is, in fact, observed. On the other hand, the introduction of 2-CH₃ substituents in benzene, as in xylenes, increases the π electron donating capacity of these compounds considerably while at the same time the steric repulsion between the bulky –CH₃ groups and the atoms of 1,2-dichloroethane is also increased. This should give rise to higher H° values as has indeed been observed. Within the xylenes, the steric repulsion for p-xylene would be minimum, so that H° for the 1,2-dichloroethane + p-xylene mixture should be less than that of 1,2-dichloroethane + o-xylene or m-xylene mixtures has also been observed. It thus appears that charge transfer and steric hinderance are the predominant factors that characterize these mixtures.
Further, the observed $H^E$ data for 1,2-dichloroethane + aniline mixtures may be accounted for if we assume

i) that aniline is present as r-mers and monomers, and there is a decrease in self association of r-mers when it is mixed with 1,2-dichloroethane,

ii) that there is a specific interaction between aniline and 1,2-dichloroethane;

iii) that there is a steric repulsion between aniline and the bulky chlorine atoms of 1,2-dichloroethane.

Since the observed $H^E$ is the cumulative effect of the contributions due to factors (i), (ii) and (iii), the positive $H^E$ values indicate that the factors (i) and (iii) outweigh (ii) in the present situation.

The experimental $H^E$ data for 1,2-dichloroethane + aromatic hydrocarbon mixtures were analysed in the light of the following theories.

1. Flory's Theory
2. Sanchez and Lacombe's Theory

1. Flory's Theory:

$H^E$ according to this theory is given by $^{45-46}

$$H^E = x_1 p^*_1 v^*_1 \left[ \left(1/v_1\right) - \left(1/v_{\text{calc}}\right) \right] + x_2 p^*_2 v^*_2 \times \left[ \left(1/v_2\right) - \left(1/v_{\text{calc}}\right) \right] + x_1 v^*_1 \Theta_2 x_{12}/v_{\text{calc}} \quad (4.9)$$

where

$v_{\text{calc}} = v_o + v_{\text{calc}}^E$
\[ \tilde{V}^{E}_{\text{calc}} = \tilde{V}_{o}^{7/3} \left( \frac{4}{3} - \frac{1}{3} \right)^{-1} (\tilde{T} - \tilde{T}_{o}) \]

and \( \tilde{V}_{o}, \tilde{T}, \) and \( \tilde{T}_{o} \) have the same significance as described by Flory and were evaluated as described in Chapter 2 (equations 2.7, 2.8 and 2.12). The reduced temperature, \( \tilde{T} \), of the mixture is dependent on the adjustable parameter \( \Theta_{x_{12}} \) (Chapter 2, equation 2.12). \( \Theta_{x_{12}} \) was evaluated by using the \( H_{\text{exp}}^{E} \) values at equimolar composition for a particular system by fitting in the equation (4.9). \( H_{\text{calc}}^{E} \) values were, then, obtained at \( x_{1} = 0.3 \) and 0.7 and these are recorded in Table 4-3. A comparison of the \( H_{\text{calc}}^{E} \) and \( H_{\text{exp}}^{E} \) values at 298.15 for these mixtures shows that Flory's theory correctly predicts the sign of \( H^{E} \) but the quantitative agreement is not very good. At 308.15 and 318.15K, the sign for \( H^{E} \) is correct only at \( x_{1} = 0.7 \), while the sign of \( (\partial H^{E}/\partial T) \) is predicted correctly for all the mixtures.

2. Sanchez and Lacorabe's Theory:

The \( H^{E} \) data for the various mixtures were next examined for Sanchez and Lacorabe's theory. \( H^{E} \), according to this theory, is given by

\[ H^{E} = 2r_{\text{mix}} \tilde{\varrho}_{1} \phi_{1} \phi_{2} (\tilde{\varrho}_{1}^{*} + \tilde{\varrho}_{2}^{*} - 2 \tilde{\varrho}_{12}^{*}) + Rr_{\text{mix}} T \]

\[ \left\{ \left( \frac{\phi_{1}^{*}}{T_{1}} - \frac{\varrho_{1}^{*}}{T_{12}} \right) + \left( \frac{\phi_{2}^{*}}{T_{2}} - \frac{\varrho_{2}^{*}}{T_{12}} \right) \right\}^{2} + pV^{E} \]

where the various terms have their usual significance and were evaluated as described in Chapter 1. A knowledge of
Comparison of $H^E$ values calculated according to Flory's Theory with the corresponding experimental values for the various mixtures at three mole fractions of 1,2-dichloroethane ($l$) at various temperatures.

<table>
<thead>
<tr>
<th>System</th>
<th>Mole fraction of $l$</th>
<th>$H^E$ (J mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>298.15K</td>
</tr>
<tr>
<td>1,2-Dichloroethane +</td>
<td>0.3</td>
<td>3.10</td>
</tr>
<tr>
<td>benzene</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>5.4</td>
</tr>
<tr>
<td>1,2-Dichloroethane +</td>
<td>0.3</td>
<td>-12.8</td>
</tr>
<tr>
<td>toluene</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>3.3</td>
</tr>
<tr>
<td>1,2-Dichloroethane +</td>
<td>0.3</td>
<td>-10.2</td>
</tr>
<tr>
<td>o-xylene</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>13.5</td>
</tr>
<tr>
<td>1,2-Dichloroethane +</td>
<td>0.3</td>
<td>-56.9</td>
</tr>
<tr>
<td>m-xylene</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>3.9</td>
</tr>
<tr>
<td>1,2-Dichloroethane +</td>
<td>0.3</td>
<td>-44.8</td>
</tr>
<tr>
<td>p-xylene</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>-36.8</td>
</tr>
</tbody>
</table>
\( \varepsilon_{\text{mix}} \) and \( \varepsilon_{12}^* \) for the mixtures is required to calculate \( H^E \) according to this theory. Since \( \varepsilon_{12}^* \) and \( \varepsilon_{\text{mix}} \) for the mixture cannot be evaluated by theoretical methods, this were calculated by fitting the experimental \( v^E \) and \( H^E \) values for an equimolar composition at 308.15K to equation (4.10 and 4.11):

\[
v^E = \left[ \frac{1}{\varepsilon_{\text{mix}}} \left( \phi_1 \tilde{\varepsilon}_1 + \phi_2 \tilde{\varepsilon}_2 \right) \right] v^E_{\text{mix}} r_{\text{mix}} \tag{4.11}
\]

The \( \varepsilon_{12}^* \) and \( \tilde{\varepsilon}_{\text{mix}} \) values thus obtained were utilised to see as to how closely equation (2.17) was satisfied. In all subsequent evaluations of \( \tilde{\varepsilon}_{\text{mix}} \) for the mixture equation 2.17 was always solved to this accuracy as stated in Chapter 2. The \( \varepsilon_{12}^* \) value thus obtained for the mixture, from its \( v^E \) and \( H^E \) values for an equimolar mixture at 308.15K was next used to calculate \( \varepsilon_{\text{mix}}^* \) and \( \tilde{\varepsilon}_{\text{mix}} \) (equation 2.19 and 2.16) and hence \( H^E \) at any temperature and composition. The \( H^E \) values so calculated are recorded in Table 4-4 and are also compared with the corresponding experimental \( H^E \) values. An examination of Table 4-4 reveals that the theoretical \( H^E \) values compare well with the corresponding experimental values.

The sign and magnitude of \( H^E \) depends primarily on the contribution of the terms in (4.10). Since the contribution of the first term in equation (4.10), which depends on \( X_{12} \) (Table 4-4), outweighs those due to \( \sum_i \left( \tilde{\varepsilon}_i \phi_i \tilde{\phi}_i \right) / T_i \), \( H^E \) is negative. This is true for all except the binary mixtures of 1,2-dichloroethane with benzene. This may be attributed to the small negative \( X_{12} \) value for this mixture which suggests, that in this mixture the unlike interactions are energetically more favoured than the like ones. However
TABLE 4-4

Comparison of $H^E$ values calculated from Sanchez and Lacombe's Theory with the corresponding values for the various mixtures at three mole fractions of 1,2-dichloroethane (A) at various temperatures. Also included are the $\chi_{12}$ and $\xi$ values for these mixtures.

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>1,2-Dichloroethane + bengene</td>
<td>0.3</td>
<td>-116.1</td>
<td>41.7</td>
<td>-72.3</td>
<td>39.7</td>
<td>-182.3</td>
<td>46.2</td>
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</tr>
<tr>
<td></td>
<td>0.5</td>
<td>68.0</td>
<td>65.1</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td>0.7</td>
<td>47.3</td>
<td>79.0</td>
<td>49.0</td>
<td>55.1</td>
<td>29.5</td>
<td>74.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\chi_{12} = \frac{-3.4}{(\text{Cal mol}^{-1})}$</td>
<td>$\xi = 1.002$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2-Dichloroethane + toluene</td>
<td>0.3</td>
<td>-22.3</td>
<td>-8.5</td>
<td>-42.3</td>
<td>-40.0</td>
<td>-29.9</td>
<td>-34.6</td>
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<td>0.5</td>
<td>21</td>
<td>-26.9</td>
<td>-</td>
<td>-</td>
<td>33.3</td>
<td>-5.2</td>
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<tr>
<td></td>
<td>0.7</td>
<td>38.8</td>
<td>21.9</td>
<td>50.0</td>
<td>31.0</td>
<td>77.9</td>
<td>40.5</td>
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<tr>
<td></td>
<td></td>
<td>$\chi_{12} = \frac{27.52}{(\text{Cal mol}^{-1})}$</td>
<td>$\xi = 0.988$</td>
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<tr>
<td>1,2-Dichloroethane + o-xylene</td>
<td>0.3</td>
<td>-6.5</td>
<td>-65.3</td>
<td>27.3</td>
<td>-38.5</td>
<td>11.2</td>
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<td>-19.3</td>
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<td>$\chi_{12} = \frac{48.36}{(\text{Cal mol}^{-1})}$</td>
<td>$\xi = 0.980$</td>
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<tr>
<td>1,2-Dichloroethane + m-xylene</td>
<td>0.3</td>
<td>-48.6</td>
<td>-50.0</td>
<td>-37.2</td>
<td>-25.0</td>
<td>-31.8</td>
<td>-4.2</td>
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<tr>
<td></td>
<td>0.5</td>
<td>9.5</td>
<td>15.1</td>
<td>-</td>
<td>-</td>
<td>53.9</td>
<td>68.0</td>
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<td></td>
<td>0.7</td>
<td>37.0</td>
<td>95.0</td>
<td>128.1</td>
<td>110.9</td>
<td>149.3</td>
<td>129.0</td>
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<tr>
<td></td>
<td></td>
<td>$\chi_{12} = \frac{43.39}{(\text{Cal mol}^{-1})}$</td>
<td>$\xi = 0.981$</td>
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<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

*$\chi_{12}$ and $\xi$ are dimensionless. $\ell = 0.988$ (Cal mol$^{-1}$)
1,2-Dichloroethane + p-xylene

\[
\begin{array}{cccccccccc}
& 0.3 & -120.1 & -99.0 & -70.3 & -68.9 & -98.8 & -56.4 & \\
p-xylene & 0.5 & -63.2 & -64.5 & - & -31.4 & -5.1 & & \\
& 0.7 & 33.8 & 17.4 & 41.6 & 55.5 & 65.5 & 71.3 & \\
\end{array}
\]

\[
X_{12} = 40.52 \quad \eta = 0.983
\]

1 calorie = 4.184 Joules
the close proximity of two Cl atoms of 1,2-dichloroethane in its interactions with the π electrons of the benzene ring, and give rise to a repulsive contribution, and since the observed $H^E$ is the cumulative sum of the contributions due to the unii and steric interactions, $H^E$ for this mixture is positive.

It would now be instructive to see as to how the interaction energies $\epsilon_{12}$ in these 1,2-dichloroethane and aromatic hydrocarbons mixtures deviate from the geometric mean law. For this purpose we evaluated $\xi$ from

$$\xi = \epsilon_{12} / (\epsilon_{11}^* \epsilon_{22}^*)^{1/2}$$

and these $\xi$ values are recorded in table 4-1. An examination of this table reveals that among all the binary mixtures, unlike interactions in 1,2-dichloroethane + benzene are energetically more favourable than the like ones. The introduction of -CH$_3$ substituents in benzene would cause the charge transfer interaction and the steric repulsion between 1,2-dichloroethane and toluene and xylenes to increase in the order

$$\text{xylene} \succ \text{toluene},$$

so that the unlike interactions in 1,2-dichloroethane + toluene (although weaker than those in 1,2-dichloroethane + benzene) should be energetically more favourable than those in 1,2-dichloroethane + xylene mixtures. The thermodynamic studies on 1,2-dichloroethane + aromatic hydrocarbon mixtures have thus revealed that these mixtures are characterised by specific interactions between the components of these mixtures and as the number of -CH$_3$ substituents in benzene increases the
aromatic hydrocarbon goes away from 1,2-dichloroethane in these binary mixtures.

Yadav et al.\textsuperscript{48}a have recently performed dielectric studies on binary mixture of non-electrolytes and have observed that the induced dipole moment varies inversely with the distance of separation between the components of the binary mixture in the complexed state. It was, therefore, thought worthwhile to perform dielectric studies on these mixtures.

Since aniline is self associated it was thought worthwhile to analyse the data for 1,2-dichloroethane (A)+aniline (B\textsubscript{n}) mixtures in terms of the ideal associated model of non-electrolytes.\textsuperscript{49-50}

It was assumed that in this mixture (aniline is designated as B\textsubscript{n} since aniline is self associated and 1,2-dichloroethane as A) mutual equilibrium of species A\textsubscript{k}B\textsubscript{k} A\textsubscript{m}B\textsubscript{x} and B\textsubscript{l} (where l = 1,2,3...l, m = 1,2,3...m, k = 1,2,3...k, x = 1,2,3...x) exists as shown by the reaction

\[
A + B_n \rightarrow A_k B_k + A_m B_x + B_l
\]  

so that the equilibrium constants for the various association reactions are represented by the equation (4.12) are

\[
K_{k,k/n} = \frac{a_{A_k B_k}}{a_A^k a_{B_n}^{k/n}} \quad (4.13)
\]

\[
K_{m,x/n} = \frac{a_{A_m B_x}}{a_A^m a_{B_n}^{x/n}} \quad (4.14)
\]

and

\[
K_{l,n} = \frac{a_{B_l}}{a_{B_n}^{1/n}} \quad (4.15)
\]
where 'a' are the activities of the respective species. If the activity coefficients of the various species represented in equation (4.12) are assumed to be unity,$^{19-51}$ the material balance equation for the system can be written as

\[
a_A + a_B + \sum_k K_{k,n} \frac{a^k_{A}}{a_{B}^n} + \sum_m K_{m,n} \frac{a^m_A}{a_{B}^n} + \sum_l K_{l,n} \frac{1}{a_{B}^n} = 1.
\]

(4.16)

we first considered the following cases:

**Ist case**

where \( n = 2, k = m = 1, x = 2 \)

so \( A + B_2 \rightleftharpoons AB + A_2B + B \) (4.17)

**IInd case**

where \( n = m = 2, k = x = 1 = 1 \)

so \( A + B_2 \rightleftharpoons AB + A_2B + B \) (4.18)

The material balance equation for these cases reduced to

**Ist case**

\[
a_A + a_{B_2} + K_{1,0.5} a_{A}^{0.5} a_{B}^{0.5} + K_{1,1} a_{A} a_{B_2} + K_{0.5} a_{B_2}^{0.5} = 1
\]

(4.19)

**IInd case**

\[
a_A + a_{B_2} + K_{1,0.5} a_{A}^{0.5} a_{B}^{0.5} + K_{2,0.5} a_{A}^2 a_{B_2}^{0.5} + K_{2} a_{B_2}^{0.5} = 1
\]

(4.20)
Algebraic manipulation of equation (4.19) and equation (4.20) yielded

\[ K_{1,0.5} a_A + K_{1,1} a_B^2 + K_{0.5} = \frac{(1-a_A-a_B)}{a_B^2} \] (4.21)

\[ K_{1,0.5} a_A + K_{2,0.5} a_A^2 + K_{0.5} = \frac{(1-a_A-a_B)}{a_B^2} \] (4.22)

In order to evaluate the various equilibrium constants in the equations (4.21 and 4.22), the observed activities of the components of these binary mixtures were corrected for dispersion contributions by expressing

\[ a_A = \frac{\nu_A x_A}{\nu_A^*} \] (4.23)

\[ a_B = \frac{\nu_B x_B}{\nu_B^*} \] (4.24)

where \( \nu_A^* \) and \( \nu_B^* \) are the activity coefficients of a reference mixture. Since cyclohexane is inert in nature and has nearly the same molar volumes as that of 1,2-dichloroethane, cyclohexane (A) + aniline (B) was taken as the reference system for the present analysis. A series of values were next assumed for the equilibrium constants in equation (4.21 and 4.22) and the process was repeated till a set of K values was obtained which yielded \( D_{\text{calc}} \) which corresponded very closely to \( D_{\exp} \) values i.e. those obtained from the experimental \( a_A \) and \( a_B \) values with the help of equation

\[ \frac{(1-a_A-a_B)}{a_B^2} = D \] (4.25)

The equilibrium constants for both the cases are given in Table 4-5. The activity coefficient data for cyclohexane + aniline mixtures were taken from the literature while the
Equilibrium constants $K$ and enthalpy of formation $\Delta H$, for the various molecular species in the mixture 1,2-dichloroethane ($A$) + aniline ($B_n$).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Property</th>
<th>$A_B$</th>
<th>$A_{B_2}$</th>
<th>$A_{2B}$</th>
<th>$A_{2B_2}$</th>
<th>$B$</th>
<th>$\Delta^2 D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A + B_2 \rightarrow A_B + A_{B_2} + B$</td>
<td>$K$</td>
<td>0.300</td>
<td>0.325</td>
<td>-</td>
<td>0.150</td>
<td>0.0096</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\Delta H$</td>
<td>-5.00</td>
<td>-8.00</td>
<td>-</td>
<td>0.01</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$KJ/mol$</td>
<td>-</td>
<td>0.05</td>
<td>-</td>
<td>0.40</td>
<td>0.0143</td>
<td></td>
</tr>
<tr>
<td>$A + B_2 \rightarrow A_B + A_{2B} + B$</td>
<td>$K$</td>
<td>0.05</td>
<td>-</td>
<td>0.05</td>
<td>0.40</td>
<td>0.0143</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\Delta H$</td>
<td>-50.0</td>
<td>-25.00</td>
<td>-</td>
<td>0.10</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$KJ/mol$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$A + B_2 \rightarrow A_{2B} + A_{2B_2}$</td>
<td>$K$</td>
<td>-</td>
<td>-</td>
<td>2.39</td>
<td>16.72</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\Delta H$</td>
<td>-</td>
<td>-</td>
<td>-5.78</td>
<td>-5.11</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$KJ/mol$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
activity coefficients for 1,2-dichloroethane + aniline system were determined by the measurements of their vapour pressures by Barker's method.\textsuperscript{55a}

The criterion of effectiveness was the variance of fit, \( \sigma^2_D \) defined by

\[
\sigma^2_D = \frac{\sum_q (D_{\text{calc}} - D_{\text{exp}})^2}{q - p}
\]  \( (4.26) \)

where \( q \) is the number of observations used in the fit and \( p \) is the number of adjustable parameters. Since \( \sigma^2_D \) for both the cases is small, (given Table 4-5) this analysis of the activity coefficient data thus suggests the presence of either \( AB, AB_2, \) and \( B \) or \( AB, A_2B, \) and \( B \) molecular species in the mixture. We, therefore, further analysed our \( H^E \) data in terms of the above two models, where \( H^E \) was expressed as

\textbf{1st case}

\[
H^E = \frac{(n_{AB} \Delta H_{AB} + n_{AB_2} \Delta H_{AB_2} + n_B \Delta H_B)}{(N_A + N_B)}
\]  \( (4.27) \)

\textbf{2nd case}

\[
H^E = \frac{(n_{AB} \Delta H_{AB} + n_{A_2B} \Delta H_{A_2B} + n_B \Delta H_B)}{(N_A + N_{B_2})}
\]  \( (4.28) \)

where \( n_{AB}, n_{AB_2}, n_{A_2B}, \) and \( n_B \) are the number of moles of \( AB, AB_2, A_2B, \) and \( B \) species present at equilibrium in solution and \( N_A \) and \( N_{B_2} \) are the stoichiometric amounts of \( A \) and \( B_2. \) If the equilibrium molefraction of \( A, B_2, AB, AB_2 \) and \( B \) are represented by \( Z_A, Z_{B_2}, Z_{AB}, Z_{AB_2}, \) and \( Z_B \) then for an ideal associated mixture \( A + B_2 \) containing \( AB, AB_2 \) and \( B \) molecular
species

$$Z_A + Z_{B_2} + Z_{A\beta} + Z_{A\beta B_2} + Z_B = 1 \quad (4.29)$$

where

$$Z_{A\beta} = K_{1,0.5} Z_A^{1/2} \quad ; \quad Z_{A\beta B_2} = K_{1,1} Z_A Z_{B_2} \quad ;$$

$$Z_B = K_{0.5} Z_{B_2}^{1/2}$$

The experimental $H^E$ values were again corrected for dispersion contributions by substracting $H^E_{\text{exp}}$ values for aniline + cyclohexane mixture at 308.15K from $H^E_{\text{exp}}$ values of 1,2-dichloroethane + aniline mixture. As a result, the $H^E$ in equations (4.27) and (4.28) is given by:

$$H^E = H^E_{\text{exp}} - H^E_{\text{aniline + cyclohexane}} \quad (4.30)$$

Algebraic manipulation of equation (4.27) and (4.28) and the material balance equations (4.21) and (4.22) along with

$$N_A = n_A + n_{A\beta} + n_{A\beta B_2} \quad (4.31)$$

$$N_{B_2} = n_{B_2} + \frac{1}{2} n_{A\beta} + \frac{1}{2} n_B + n_{A\beta B_2} \quad (4.32)$$

lead to:

$$J_{H^E} = K_{1,0.5} Z_A \Delta H_{A\beta} + K_{1,1} Z_A \Delta H_{A\beta B_2} + K_{0.5} Z_{B_2}^{1/2} \Delta H_B \quad (4.33)$$

where

$$J = (Z_{B_2}^{1/2} + 0.5 K_{0.5} + 0.5 K_{1,0.5} Z_A + K_{1,1} Z_{B_2}^{1/2})/x_{B_2} \quad (4.34)$$
Further combination of (4.29 - 4.32) gives

\[ x_{B_2} = \frac{Z_{B_2} + 0.5K_1^1,1,0.5Z_{B_2} + 0.5K_1^1,0.5Z_{B_2}}{Z_A^1 + Z_{B_2} + 0.5K_1^1,1,0.5Z_{B_2} + 1.5K_1^1,0.5Z_{A,B_2}^2} \]  \( (4.35) \)

where

\[ z_A = \frac{1-Z_{B_2} - K_1^0.5Z_{B_2}^3}{1+K_1^0.5Z_{B_2} + K_1^1Z_{B_2}} \]  \( (4.36) \)

Applying a similar process to the II case when the mixture contains \( AB^+ , \ \Lambda_2B^+ \), molecular species, the final expression was

\[ JH = K_1^1,0.5Z_A^1 \Delta H_{A,B} + K_2^2,0.5Z_{A,B_2}^1 \Delta H_{A,B} + K_0^0.5 \Delta H \]  \( (4.37) \)

where

\[ J = (Z_{B_2} + 0.5K_1,0.5Z_{A,B} + 0.5K_2^2,0.5Z_{A,B_2} + 0.5K_0,0.5) / x_{B_2} \].

\( (4.38) \)

Also

\[ x_{B_2} = \frac{Z_{B_2} + K_1^0.5Z_A^1 Z_{B_2}^3 + 0.5K_2^2,0.5Z_{A,B_2}^1 + 0.5K_0,0.5Z_{B_2}^2}{Z_A^1 + Z_{B_2} + 1.5K_1^0.5Z_{A,B_2}^1 + 0.5K_0,0.5Z_{B_2}^2} \]  \( (4.39) \)

and

\[ z_{B_2} = \frac{1}{2} \frac{(K_1^1,0.5Z_A^1 + K_2^2,0.5Z_{A,B_2}^1)^{1/2}}{z_{A,B_2}^1} \sqrt{(K_1^1,0.5Z_A^1 + K_2^2,0.5Z_{A,B_2}^1)^2 - 4(z_A^1 - 1)} \]  \( (4.40) \)

where \( z_{A,B} \), \( z_{A,B_2} \) and \( z_B \) are defined by

\[ Z_{A,B} = K_1^1,0.5Z_A^1 z_{B_2}^3 \quad Z_{A,B_2} = K_2^2,0.5Z_{A,B_2}^1 z_{B_2}^3 \quad Z_B = K_0^0,0.5z_{B_2}^4 \].
using the various \( K \) values (given in table 4-5) we calculated \( x_{B_2} \) for the case I by assuming different values of \( Z_A \) and assigned various values to \( \Delta H_{AB}, \Delta H_{A, B_2} \) and \( \Delta H_B \) till they gave \( H^E \) values (for equation 4.29 and 4.37) that compared well with the corresponding experimental values. The various \( \Delta H \) values are recorded in Table 4-5 and the calculated \( H^E \) values are compared with \( H^E_{\text{exp}} \) values as shown in figure 4-XI.

Similarly the \( x_{B_2} \) values for case II were calculated and \( \Delta H_{AB}, \Delta H_{A_2B} \) and \( \Delta H_B \) were assigned various values till they gave values comparable to \( H^E_{\text{exp}} \) values. However, the \( H^E_{\text{exp}} \) values so calculated for both the cases did not compare very well with those determined experimentally (\( H^E_{\text{exp}} \)). The maximum deviation for the first case being \( \approx 150 \text{J/mol} \) and for the second case \( \approx 300 \text{J/mole} \) at about \( x_1 = 0.75 \). The very small \( \Delta H_B \) value however suggests self association of aniline in aniline+1,2-dichloroethane mixture is very small. This gets further substantiated by the observations of Bellamy and Williams that aniline is not associated.\(^{56}\)

We next assumed that aniline exists in the form of monomers so that 1,2-dichloroethane + aniline mixtures were assumed to be characterised by a reaction of the type

IIIrd case

\[
A + B \rightleftharpoons A_2 B_2 + A_2 B
\]

The material balance equation for this reaction can be written in the form

\[
K_{2,1} + K_{2,2} a_B = (1-a_A-a_B)/(a_A^2 a_B)
\]  

(4.41)
Hole fraction of aniline

Flm $V - XI$ System aniline + 1,2-dichloroethane at 368.15K

- Expt.  
- Calculated (Ideal associated model)

**Fig. 4-XI** System aniline + 1,2-dichloroethane at 368.15K

- Expt.  
- Calculated

Mole fraction of aniline

![Graph showing mole fraction of aniline](image-url)
If the theory is correct, a graph of $a_B$ versus $(1-a_A-a_B)/a_A^2a_B$ should yield a straight line, whose slope and intercept would give the values of $K_{2,2}$ and $K_{2,1}$. This is indeed true and it gave $K_{2,2} = 16.72$, $K_{2,1} = 2.39$ by the least squares method.

Further, $x_B$ and $Z_B$ were calculated by the following expression:

$$x_B = \frac{Z_B + K_{2,1}Z_A^2Z_B + 2K_{2,1}Z_A^2Z_B}{Z_A + Z_B + 3K_{2,1}Z_A^2Z_B + 4K_{2,1}Z_A^2Z_B}$$  \hspace{1cm} (4.4.2)

$$Z_B = \frac{-K_{2,1}Z_A^2 + (K_{2,1}Z_A^2 + 2K_{2,1}Z_A^2 - 4(Z_A - 1)(K_{2,1}Z_A^2) - 4K_{2,1}Z_A^2}{2K_{2,1}Z_A^2}$$  \hspace{1cm} (4.4.3)

and were substituted in the equation (4.4.4) along with the $K_{2,1}$ and $K_{2,2}$ values to yield

$$\left(\frac{1}{Z_A} + K_{2,1} + K_{2,2}Z_B\right)H^E/x_B = K_{2,1} H_{2B} + Z_B \Delta H_{12B2}$$  \hspace{1cm} (4.4.4)

If the theory, as developed above, is correct, a plot of $Z_B$ versus $\left(\frac{1}{Z_A} + K_{2,1} + K_{2,2}Z_B\right)H^E/x_B$ should yield a straight line whose intercept and slope would give values of $\Delta H_{12B}$ and $\Delta H_{2B2}$. A straight line indeed was obtained which yielded $\Delta H_{12B} = -5.78$ and $\Delta H_{2B2} = -5.11$ KJ/mol$^{-1}$ by the method of least squares.

As a further check on the values of $K_{2,1}$ and $K_{2,2}$, we carried out NMR studies of the mixture of 1,2-dichloroethane+ aniline mixtures. An equation, which related the observed shifts to equilibrium constants and limiting shifts of 1:2 and 2:2 complexes, was derived in the manner described by
Dodson et al. for 1:1 and 1:2 charge transfer complexes. The following two type of equilibriums were assumed to exist in the solution:

\[ \begin{align*}
2A + B & \rightleftharpoons A_2B \\
A_2B + B & \rightleftharpoons A_2B_2
\end{align*} \]

where \( K_{2,1} \) and \( K_{2,2} \) are the equilibrium constants and can be written as

\[ \begin{align*}
K_{2,1} &= \frac{[A_2B]}{[A][B]} \\
K_{2,2} &= \frac{[A_2B_2]}{[A_2B][B]}
\end{align*} \]

The total concentration of B was taken to be much greater than A, i.e., \([B] \gg [A]\) (where B acts as donor and A as acceptor in the formation of charge transfer complexes), to obtain a sufficient fraction of one component in the complexed state. The total absorbance at the wavelength of maximum absorption will be given for such a system by:

\[ \Lambda' = \varepsilon_A(A) + \varepsilon_{A_2B}(A_2B) + \varepsilon_{A_2B_2}(A_2B_2) \]  \( (4.47a) \)

where \( \varepsilon_A, \varepsilon_{A_2B}, \) and \( \varepsilon_{A_2B_2} \) are the molar absorptivities of the acceptor A, complex \( A_2B \) and complex \( A_2B_2 \). It was further assumed that neither A nor B absorbed at the wavelength of measurement, as suggested by Benesi and Hildebrand. This gave

\[ \Lambda' = \varepsilon_{A_2B}(A_2B) + \varepsilon_{A_2B_2}(A_2B_2) \]  \( (4.47b) \)
From equation (4.45) and (4.46),

\[(\Lambda_2 B) = K_1 (\Lambda)^2 (B) \quad (4.48)\]

\[(\Lambda_2 B_2) = K_2 ((\Lambda_2 B)(B) = K_1 K_2 (\Lambda)^2 (B)^2 \quad (4.49)\]

The assumption \[^{[B]} >> [\Lambda]\] lead to

\[\Lambda = (\Lambda) \quad (4.50)\]

and

\[\Lambda = (\Lambda) + 2(\Lambda_2 B) + 2(\Lambda_2 B_2) \quad (4.51a)\]

where \((\Lambda)\) will be equal to zero, because all the \(\Lambda\) is assumed to have complexed due to its low concentration. Therefore,

\[
\Lambda = 2(\Lambda_2 B) + 2(\Lambda_2 B_2); \quad \text{and} \quad (4.51b)
\]

from \((4.47b)\), \((4.48)\) and \((4.49)\),

\[
\Lambda' = \left\{ \xi_{\Lambda_2 B} K_1 (\Lambda)^2 [B] + \xi_{\Lambda_2 B_2} K_1 K_2 (\Lambda)^2 [B]^2 \right\}
\]

\[
= (\Lambda)^2 \left\{ \xi_{\Lambda_2 B} K_1 [B] + \xi_{\Lambda_2 B_2} K_1 K_2 [B]^2 \right\} \quad (4.52)
\]

Also, from equations \((4.51b)\), \((4.48)\) and \((4.49)\)

\[
\Lambda = 2K_1 (\Lambda)^2 [B] + 2K_2 K_1 (\Lambda)^2 [B]^2
\]

\[
(\Lambda)^2 \left\{ 2K_1 [B] + 2K_2 K_1 [B]^2 \right\} \quad (4.53)
\]

Dividing equation \((4.52)\) by \((4.53)\),

\[
\frac{\Lambda'}{[\Lambda]} = \frac{\xi_{\Lambda_2 B} K_1 [B] + \xi_{\Lambda_2 B_2} K_1 K_2 [B]^2}{2K_1 [B] + 2K_1 K_2 [B]^2} \quad (4.54)
\]

To obtain \(K\) from a series of measurements of \(\Lambda\) for various values of \([B]\), an expression algebraically
equivalent to equation (4.54) i.e. equation (4.55) was used.

\[ \Delta \text{obs.} = \frac{\Delta(1)K_{2,1}^2[B] + \Delta(2)K_{2,1}K_{2,2}^2[B]^2}{2K_{2,1}^2[B] + 2K_{2,1}K_{2,2}^2[B]^2} \]  

where \(K_{2,1}^2\) and \(K_{2,2}^2\) have the usual meaning, and \(\Delta(1)\) is the chemical shift of the measured nucleus in the complex \(A_2B\), relative to the chemical shift of the same nucleus in pure 1,2-dichloroethane, all in solution and \(\Delta(2)\) is the corresponding value for the complex \(A_2B_2^*\).

Evaluation of \(K_{2,1}^2\) and \(K_{2,2}^2\), \(\Delta(1)\), and \(\Delta(2)\) from equation 4.55 required an NMR study to be made on 1,2-dichloroethane + aniline mixtures. For this purpose we prepared dilute solutions of 1,2-dichloroethane in aniline. All these solutions were prepared by mixing aniline and 1,2-dichloroethane (by weight) in the NMR tubes, followed by the addition of a fixed quantity of cyclohexane which was used as the internal reference. The proton chemical shifts of 1,2-dichloroethane protons relative to cyclohexane were detected on a Varian HR-60 NMR Spectrophotometer using the side band method. The chemical shifts for 1,2-dichloroethane protons were averaged over three determinations and were reproducible to within ±0.5 Hz. All these values are recorded in Table 4-6.

For quantitative evaluation of the various parameters in 4.55 we assumed certain values of \(K_{2,1}^2\), \(K_{2,2}^2\), \(\Delta(1)\) and \(\Delta(2)\) which were then refined through an iterative
TABLE 4-6

Comparison of experimental shifts of 1,2-dichloroethane protons with those calculated from equation (4.55) and equilibrium constants for the mixture of 1,2-dichloroethane + aniline.

<table>
<thead>
<tr>
<th>Mole fraction of 1,2-dichloroethane</th>
<th>$\Delta_{\text{expt.}}$</th>
<th>$\Delta_{\text{calc.}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0521</td>
<td>-0.321</td>
<td>-0.312</td>
</tr>
<tr>
<td>0.0804</td>
<td>-0.302</td>
<td>-0.302</td>
</tr>
<tr>
<td>0.0936</td>
<td>-0.284</td>
<td>-0.284</td>
</tr>
<tr>
<td>0.1243</td>
<td>-0.266</td>
<td>-0.268</td>
</tr>
<tr>
<td>0.1411</td>
<td>-0.259</td>
<td>-0.263</td>
</tr>
<tr>
<td>0.1726</td>
<td>-0.240</td>
<td>-0.247</td>
</tr>
<tr>
<td>0.1986</td>
<td>-0.230</td>
<td>-0.236</td>
</tr>
</tbody>
</table>

$K_{2,1} = 0.02$, $K_{2,2} = 0.43^2$, $\Delta(1) = 0.43$, $\Delta^o(2) = 10.71$
process. The values of the best fit are given in Table 4-6 along with \( \Delta_{\text{obs}} \) and \( \Delta_{\text{calc}} \), \( K_{2,1} \) and \( K_{2,2} \). The values of \( K_{2,1} \) and \( K_{2,2} \) on conversion to mole fractions \( K \) for the special case under consideration, yielded \( K_{2,1} = 0.92 \) and \( K_{2,2} = 0.012 \). These \( K \) values are in reasonably good agreement with those obtained thermodynamically (\( K_{2,1} = 2.39 \) and \( K_{2,2} = 16.72 \)).
REFERENCES


46. P. J. Flory and A. Abe, ibid, 87, 1838 (1965).


