The contact interaction parameters $X_{ij}$ have been evaluated for six ethyl acetate + hydrocarbon mixtures from the heat of mixing data obtained calorimetrically. The component 1 is $n$-pentane, $n$-heptane, $n$-octane, $n$-hexadecane, cyclohexane or isooctane. The calculations were based on the statistical theory of liquid mixtures developed by Flory. The observed variations in $X_{12}$ or $X_{12}/S_1$ have been explained by the energetic effects associated with a correlation of molecular orientations in the pure components and the mixtures and the dipole induced dipole interactions between the ester and the hydrocarbons.

It is now believed that the contact interaction in non-polar mixtures of $n$-alkanes arises from two effects, viz. (i) a positive contribution from the difference in force fields of the two species associated with their difference in chemical nature and (ii) a positive contribution arising from a correlation of molecular orientations in the pure components and the mixture. If on the other hand, $n$-alkanes are mixed with a polar component like ethyl acetate, one can expect a third contribution arising out of dipole-induced dipole interaction. It would be more appropriate as suggested by Patterson to use $X_{12}/S_1$ for comparison, particularly when systems of very different molecular surface/volume ratios are studied.

Following Patterson,

$$X_{12}/S_1 = X_{12}/S_1 \text{ (dispersion forces)} + X_{12}/S_1 \text{ (dipolar forces)} \cdot$$

$$+ X_{12}/S_1 \text{ (orientation)} \quad \ldots (1)$$

Here, the first term merely depends upon the difference of chemical nature of components in solution and not on their size or shape, and would therefore be independent of chainlength of the solvent molecules. The second term whose contribution is negative, becomes more negative as the size of the alkane increases since the polarizability increases with the chainlength of the alkanes.

The third term on the other hand can be different for molecules of the same chemical nature but of different chainlengths or shapes. The first term appears to be the major contributor for all hydrocarbon + ester mixtures. The third term becomes significant in the case of ester and $n$-hexadecane mixture.

Materials and Methods

Ethyl acetate (BDH, LR) was further purified by the procedure given by Weissberger. The solvents, $n$-pentane, $n$-heptane and cyclohexane were of AR grade (E. Merck or BDH). These were dried and fractionally distilled. Octane (98%, Schuchardt Munchen, Germany) and isooctane (Reachim, USSR) were fractionally distilled and used without further purification. Hexadecane (Fluka AG) was used as such. Its reported purity was $>99\%$. The purity of all the samples was tested by either GLC or by measuring their physical constants. Table 1 gives the quantities necessary for the application of the theory, some of which were measured in the present work.

For ethyl acetate the reduction parameters for volume ($V^*$ and $V^*$) and temperature ($T^*$) were calculated from densities at various temperatures measured by us. The reduction parameter for pressure ($P^*$) was calculated from the data on adiabatic compressibility and heat capacity. For solvents, $V^*$, $V^*$ and $T^*$ were calculated from the data on densities at various temperatures and $P^*$ values were obtained from ref. 7. The surface area/volume, $S_2$ for ester was calculated as per Flory's procedure, taking it as a right cylinder similar to $n$-alkanes, with five main chain atoms. For solvents, these values were obtained from ref. 7.

Enthalpies of mixing were measured at $30^\circ$ for the systems listed in Table 2. The instrument used was a Tian Calvet monocal conduction calorimeter fabricated by us. The details of its working principle, calibration constants of the apparatus,
### Table 2 — Heats of Mixing Data for the Systems at 30°

<table>
<thead>
<tr>
<th>System</th>
<th>( C_0 ) J mole(^{-1} )</th>
<th>( C_1 ) J mole(^{-1} )</th>
<th>( C_2 ) J mole(^{-1} )</th>
<th>( \sigma ) J mole(^{-1} )</th>
<th>( \Delta h_m ) J mole(^{-1} )</th>
<th>( \Delta h_v ) J cm(^{-3} )</th>
<th>( X_{1S} ) J cm(^{-3} )</th>
<th>( X_{2S} ) J cm(^{-3} )</th>
<th>( X_{1S}/S_i ) A(^{-1} )</th>
<th>( X_{2S}/S_i ) A(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl acetate +</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( n-C_6 )</td>
<td>4882.0</td>
<td>-952.8</td>
<td>2650.8</td>
<td>16.23</td>
<td>1200.7</td>
<td>15.16</td>
<td>52.6</td>
<td>57.94</td>
<td>48.7</td>
<td>46.7</td>
</tr>
<tr>
<td>( n-C_7 )</td>
<td>5363.7</td>
<td>-727.5</td>
<td>1889.6</td>
<td>12.49</td>
<td>1253.6</td>
<td>14.10</td>
<td>48.1</td>
<td>57.2</td>
<td>48.1</td>
<td>46.1</td>
</tr>
<tr>
<td>( n-C_8 )</td>
<td>6467.6</td>
<td>1407.8</td>
<td>-941.98</td>
<td>28.2</td>
<td>1573.2</td>
<td>16.80</td>
<td>61.8</td>
<td>75.0</td>
<td>63.1</td>
<td>60.5</td>
</tr>
<tr>
<td>( n-C_16 )</td>
<td>9355.8</td>
<td>3777.7</td>
<td>-2169.6</td>
<td>18.1</td>
<td>1932.4</td>
<td>17.09</td>
<td>60.7</td>
<td>80.2</td>
<td>67.5</td>
<td>64.7</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>5237.9</td>
<td>-432.0</td>
<td>1499.6</td>
<td>14.83</td>
<td>1298.2</td>
<td>16.47</td>
<td>54.8</td>
<td>70.1</td>
<td>58.9</td>
<td>56.5</td>
</tr>
<tr>
<td>Isooctane</td>
<td>4842.3</td>
<td>707.2</td>
<td>2254.6</td>
<td>7.42</td>
<td>1204.3</td>
<td>12.81</td>
<td>40.2</td>
<td>59.1</td>
<td>49.7</td>
<td>47.6</td>
</tr>
</tbody>
</table>

Fig. 1 — Heats of mixing for the systems, expressed per mole plotted against mole fraction of ethyl acetate. ([()] \( n \)-pentane, (\( \triangle \)) \( n \)-heptane, (\( \bullet \)) \( n \)-octane, (\( \square \)) \( n \)-hexadecane, (\( \blacktriangle \)) cyclohexane, (\( \times \)) isooctane)
filling procedure, accuracy, etc. have been described in our earlier work. We believe the accuracy to be ±2% for most of the systems.

**Results and Discussion**

Eq. (2) was fitted to the molar heats at different concentrations.

\[ \Delta h_m = x_1 x_2 \sum_{i=0}^{\infty} C_i (x_1 - x_2)^i \]  

(2)

The constants are listed in Table 2. Molar quantities however are not ideally suited for comparisons of systems with widely different molar volumes. It is more appropriate to choose heat per unit hard core volumes, \( \Delta h_v \)

\[ \Delta h_v = \Delta h_m \frac{\Delta h_m}{x_1 V_1^* + x_2 V_2^*} \]  

(3)

The contact interaction parameter \( X_{12} \) can be evaluated using expression 4)

\[ \frac{\Delta h_m}{x_1 V_1^* + x_2 V_2^*} = \Psi_1 \theta_2 (X_{12}/P_2) \left[ -\tilde{U} + T_0 \tilde{T} \right] + C_p \left[ \Psi_1 \tilde{T}_1 + \Psi_2 \tilde{T}_2 - \tilde{T}_0 \right] \]  

(4)

where \( \tilde{U} = \Psi_1 \tilde{U}_1 + \Psi_2 \tilde{U}_2 \) and \( U^* = P^*V^* \).

The energy fraction, \( \Psi \) and surface fraction \( \theta \) are defined by Eqs. (5) and (6) respectively.

\[ \Psi_1 = \frac{x_1 U_1^*}{x_1 U_1^* + x_2 U_2^*} \]  

(5)

\[ \theta_2 = \frac{x_2 V_2^*}{x_1 V_1^* + x_2 V_2^*} \]  

(6)

where \( S_1 \) and \( S_2 \) are surface/volume ratios of the component molecules.

The first term in Eq. (4) is entirely due to the energetic weakness of (1-2) contacts, i.e. \( X_{12} \). The second term is due to a difference in 'free volume' and depends on the pure components. No simple theoretical model reproduces the experimental \( \tilde{U} \) and \( \tilde{C}_p \) of the \( n \)-alkanes. This seems to be due to the existence of orientational forces in these liquids which has been neglected in the earlier theories. The significance of \( X_{12} \) can be conveniently discussed using the Flory model.

Following Flory,

\[ \tilde{U} = -V^{-1} \tilde{U}_1 \tilde{C}_p = 4/3 \tilde{V} \tilde{V}_1^{1/3} \tilde{V}_2^{1/3} - 1 \]  

(7)

In Figs. 1 and 2 \( \Delta h_m \) and \( \Delta h_v \) are plotted against \( x_2 \) and \( \theta_2 \) respectively, where

\[ \theta_2 = \frac{x_2 V_2^*}{x_1 V_1^* + x_2 V_2^*} \]  

(10)

For major part of the composition both \( \Delta h_m \) and \( \Delta h_v \) (with the exception of \( n \)-heptane) increase with the chain length of the \( n \)-alkane. This increase can be explained if one assumes the orientational order in higher alkanes \( (n>C_8 \) and above) which is being destroyed by the addition of ethyl acetate.

![Fig. 2 — Heats of mixing for the systems, expressed per unit hard core volume and plotted against segment fraction of ethyl acetate \([(\bigcirc) n\text{-pentane}, (\bigtriangleup) n\text{-heptane}, (\bullet) n\text{-octane}, (\square) n\text{-hexadecane}, (\blacktriangle) cyclohexane, (\times) iso-octane)](image-url)
in the mixture. For \( n-C_8 \) and higher alkanes the endothermic effect associated with the destruction of orientational order outweighs the negative contributions due to free volume differences and dipole-induced dipole interactions between the components. The \( n \)-pentane and \( n \)-heptane give comparable heats revealing the absence of any significant orientational order in these liquids at room temperature. Even if there is some orientational order in these liquids it may be similar to that of ethyl acetate so that the net change of order in the mixture is negligible. Cyclohexane gives higher \( X_{12}/S_1 \) than isoctane apparently indicating a larger difference in force fields between cyclohexane and ethylacetate than between isoctane and ethyl acetate. This is consistent with \( P^*/S \) values — a measure of molecular surface energy. Cyclohexane and isoctane have similar free volumes and their \( P^*/S \) values are 570 and \( 456 \times 10^{-8} \) J cm\(^{-2}\) respectively. For ethyl acetate this value is \( \approx 470 \times 10^{-8} \) J cm\(^{-2}\). The values imply a considerable difference in strengths of force fields between the linear and cyclic molecules. This is also reflected in the heat of mixing of these liquids with ethyl acetate.

More quantitative evidence of orientational order may be obtained by eliminating the free volume term from discussion and leaving the interactional term containing the \( X_{12} \), \( X_{12}/S_1 \), \( X_{21} \), and \( X_{21}/S_2 \) parameters listed in Table 2 were evaluated using \( \Delta h_m \) or \( \Delta h_r \) values at \( \phi = 0.5 \) through Eq. (4). \( X_{12} \neq X_{21} \) as seen from Table 1 while \( X_{12}/S_1 \) and \( X_{21}/S_2 \) are very close to each other following Patterson\(^1\).

\( X_{12}/S_1 \) or \( X_{21}/S_2 \) for \( n \)-pentane, \( n \)-heptane and isoctane are similar revealing the absence of any significant contribution arising from orientational order or the effect due to dipole-induced dipole interactions. While orientational order contribution becomes significant for \( n \)-octane, both orientational and dipole-induced dipole interaction become appreciable for \( n \)-hexadecane with the result that \( X_{12}/S_1 \) increases by only about 4 J cm\(^{-3}\) from that of \( n \)-octane. Cyclohexane gives higher \( X_{12}/S_1 \) than isoctane apparently indicating a larger difference in force fields between cyclohexane and ethylacetate than between isoctane and ethyl acetate. This is consistent with \( P^*/S \) values — a measure of molecular surface energy. Cyclohexane and isoctane have similar free volumes and their \( P^*/S \) values are 570 and \( 456 \times 10^{-8} \) J cm\(^{-2}\) respectively. For ethyl acetate this value is \( \approx 470 \times 10^{-8} \) J cm\(^{-2}\). The values imply a considerable difference in strengths of force fields between the linear and cyclic molecules. This is also reflected in the heat of mixing of these liquids with ethyl acetate.

References