Thermochemical and topological investigations of ternary mixtures containing ether

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Molar excess volumes, \( V_{ijk}^E \) and ultrasonic speed \( U_{ijk} \), of 1,3-dioxolane (i) + benzene (j) or toluene or + \( \alpha- \) and + \( p-xylene \) (k) ternary mixtures have been measured by dilatometer and quartz-crystal interferometer as a function of composition at 298.15K. The measured values of ultrasonic speed have been employed to evaluate molar excess compressibilities, \( (K_{E}^s)_{ijk} \). The observed data have been analysed in terms of (i) Graph-theoretical approach (based on Moelwyn-Huggins concept) and (ii) Flory’s theory. It has been observed that \( V_{ijk}^E \) and \( (K_{E}^s)_{ijk} \) values calculated by Graph approach compare better with their corresponding experimental values than the \( V_{ijk}^E \) and \( (K_{E}^s)_{ijk} \) values evaluated by Flory theory.

Recent studies\(^{1a,1b}\) have shown that Moelwyn-Huggins concept\(^2\) of interactions between the molecular surfaces of the components of binary mixtures can be extended to evaluate molar excess volumes and molar excess enthalpies of ternary mixtures. It would be interesting to see if the same can be extended to evaluate molar excess volumes and molar excess compressibilities of 1, 3-dioxolane (i) + benzene (j) or + toluene or +\( \alpha- \) or +\( p-xylene \) (k) ternary mixtures. This prompted us to measure molar excess volume and ultrasonic speed for various (i+j+k) ternary mixtures.

Materials and Methods

1,3-Dioxolane (D) [Fluka], benzene, toluene, \( \alpha- \) and \( p-xylene \) (A R grade) were purified by standard methods\(^a\) and their purities checked by measuring their densities at 298.15 and 303.15K (for 1, 3-dioxolane) and these values agreed to within \( \pm 5 \times 10^{-3} \) g cm\(^{-3} \) with their corresponding literature values\(^b\).

Molar excess volumes, \( V_{ijk}^E \), for ternary mixtures were measured in a dilatometer in the manner described elsewhere\(^4\). The dilatometer had three limbs for three components. The change in liquid level of the dilatometer capillary was measured with a cathetometer that could read up to \( \pm 0.001 \) cm. The uncertainty in our measured \( V_{ijk}^E \) values is \( \pm 0.5 \) per cent.

Ultrasonic speed at frequency 2 MHz were measured using a quartz-crystal interferometer (Mittal Enterprises, New Delhi, India). The measuring cell was a specially designed cell in which water was circulated to maintain constant temperature.

Results

Molar excess volumes \( V_{ijk}^E \) and ultrasonic speed \( U_{ijk} \) data of \( D(i) + benzene (j) + toluene or + \alpha- \) and + \( p-xylene (k) \) ternary mixtures over the entire range of composition at 298.15K are recorded in Tables 1 and 2 respectively.

The isentropic compressibility values of the studied (i+j+k) ternary mixture were evaluated employing ultrasonic speed, \( U_{ijk} \), density (\( \rho_{ijk} \)) values using the relation (1)

\[
K_s = (\rho_{ijk} U_{ijk}^{-2})^{-1}
\]

... (1)

The density \( \rho_{ijk} \) of the mixture was calculated from the experimental \( V_{ijk}^E \) data using the expression (2)

\[
V_{ijk}^E = \sum_{i+j} \sum_{k=1} M_i \rho_{ijk} (\rho_{ijk}^{-1}) + \sum_{i+j} \sum_{k=1} M_i \rho_{ijk} (\rho_{ijk}^{-1})
\]

... (2)

where \( x_i \), \( M_i \) etc. are the mole fraction and molecular mass of component (i) of (i+j+k) mixture. The excess molar isentropic compressibilities, \( (K_s^E)_{ijk} \), were determined from equation (3)

\[
(K_s^E)_{ijk} = K_s - \sum_{i+j} \phi_i (K_s)_{ij}
\]

... (3)

where \( \phi_i \) and \( (K_s)_{ij} \) etc. are the volume fraction and isentropic compressibility of components in the ternary mixture. The calculated \( K_s \) and \( K_s^E \) values for the studied mixtures are recorded in Table 2.

Molar excess volumes, \( V_{ijk}^E \), and molar excess isentropic compressibilities, \( (K_s^E)_{ijk} \), for (i+j+k) ternary
mixture as a function of composition were fitted to Redlich-Kister equation (4)

\[
X_{\text{ijk}}(X = V \text{ or } K_{\text{ijk}}) = \left\{ \begin{array}{l}
x_i x_j \left[ \sum_{n=0}^{N} X_{\text{ijk}}^{(n)} (x_i - x_j)^n \right] \\
\quad + x_i x_k \left[ \sum_{n=0}^{N} X_{\text{ijk}}^{(n)} (x_j - x_k)^n \right] \\
\quad + x_j x_k \left[ \sum_{n=0}^{N} X_{\text{ijk}}^{(n)} (x_k - x_j)^n \right] \\
\quad + x_i x_j x_k \left[ \sum_{n=0}^{N} X_{\text{ijk}}^{(n)} (x_i - x_j - x_k)^n \right]
\end{array} \right. 
\]

(4)

where \(x_i\) and \(x_j\) are the mole fractions of the ith and jth components of (i+j+k) mixtures. \(X_{\text{ijk}}^{(n)} (n=0-2)\) etc are the parameters characteristic of \((i+j+k)\) mixture and were determined by fitting \(V_{\text{ijk}}\) and \((K_{\text{ijk}})^{0.5}\) data to Eq (5)

\[
\begin{align*}
[X_{\text{ijk}}(X = V \text{ or } K_{\text{ijk}}) - x_i x_j] \left[ \sum_{n=0}^{N} X_{\text{ijk}}^{(n)} (x_i - x_j)^n \right] \\
- x_i x_j \left[ \sum_{n=0}^{N} X_{\text{ijk}}^{(n)} (x_j - x_i)^n \right] \\
= X_{ij}^0 + X_{ik}^{0.5} (x_i - x_k) x_j + X_{jk}^{0.5} (x_j - x_k) x_i \\
\end{align*}
\]

(5)

by least squares method. These parameters, along with the standard deviation, \(\sigma(X_{\text{ijk}}^E)\), defined by

\[
\sigma(X_{\text{ijk}}^E (X = V \text{ or } K_{\text{ijk}}) = \left[ \frac{\sigma(X_{\text{ijk}}(\text{expt}) - X_{\text{ijk}}(\text{calcd, Eq 4) \times 10^3}}{m} \right] \right.
\]

(6)

where \(X_{\text{ijk}}(\text{calcd, Eq 4})\) are the values evaluated from Eq. (4); \(m\) is the number of data points and \(n\) the number of adjustable parameters in Eq. (1) are recorded in Tables 1 and 2.

**Discussion**

We are unaware of any \(V_{\text{ijk}}^E\) and \((K_{\text{ijk}})^{0.5}\) data for the \(D(i) + \text{benzene (j)} \text{ or } + \text{toluene or } + \text{o-} \text{or } + \text{p-xylene (k) ternary mixtures with which to compare our results. However, there is good agreement between the theoretically observed and literature values of ultrasonic speeds for pure components [benzene : 1299.6 ms}^{-1} (1298.9)\), toluene: 1305.0 ms}^{-1} (1304.0)\), o-xylene: 1343.8 ms}^{-1} (1345.0)\), p-xylene: 1310.2 ms}^{-1} (1309.6)\].

The observed data for these mixtures were analysed in terms of the Graph-theoretical approach.

**Conceptual aspect of the Graph approach and results**

Recent studies\(^5\) have shown that \(D(i)\) in the pure state exists as monomer and \(D(i) + \text{benzene or +toluene or } + \text{o-} \text{or } + \text{p-xylene (j) binary mixtures are characterized by specific interactions between delocalised \(\pi\)-electron cloud of benzene or toluene or \(o-\) or \(p\)-xylene and \(\pi\)-electrons of cyclic ether oxygen atoms of \(D(i)\). Consequently, overall changes in molar property \((X = V \text{ or } H)\) due to these interactions were expressed\(^5\) by Eq (7)

\[
X^E = [(x_i x_j V_j) / \Sigma x_i V_i] (X_{ij} + x_j X_{12}) \\
\]

(7)

where \(X_{ij}\) and \(X_{12}\) are the molar volume and molar enthalpy interaction parameters. Since \(X^E (X = V \text{ or } H)\) data of these binary mixtures were reproduced by employing \(X_{ij}\) \(X_{12}\) parameters and \(H^E\) data (at \(x_i = 0.4 \text{ and } 0.5\)), it lends support to the assumptions made in deriving Eq (7).

If toluene or o-xylene or p-xylene (k) is added to \(D(i) + \text{benzene (j)} \text{ binary mixture, then molecular interactions in } D(i) + \text{benzene (j)} \text{ or } + \text{toluene or } + \text{o-} \text{or } + \text{p-xylene (j) ternary mixture may be assumed to involve (i) formation of (a) i-j (b) j-k and (c) i-k unlike contacts (ii) monomers of i-j and k then undergo specific interactions to yield i-j, j-k and i-k molecular entities.} \text{ If } \chi_{ij}\text{, } \chi_{ik}\text{ and } \chi_{jk}\text{ are the molar volume and molar compressibility parameters (of unlike i-j, j-k and i-k contact), then change in molar property } X(X = V \text{ or } K_{\text{ijk}}) \text{ due to process (1) [(a), (b) and (c)] would be expressible}\(^2,\(^3,\(^4\)} \text{ by Eq (8).}

\[
\Delta X_{ij}(X = V \text{ or } K_{\text{ijk}}) = \Delta x_i x_j S_j + \Delta x_j x_k S_k + \Delta x_i x_k S_i \\
\]

(8)

where \(S_i\) etc are defined by

\[
S_i = x_i V / \Sigma x_i V_i \\
\]

(9)

Further, if \(\chi_{12}\text{, } \chi_{13}\text{ and } \chi_{23}\text{ are the molar specific interaction parameters for i-j, j-k and i-k molecular entities, then change in molar volume or molar isentropic compressibility due to process (ii) would be given}\(^1\text{ by}

\[
\Delta X_i = x_i x_j x_k V_j / \Sigma x_i V_i \text{[}\chi_{ij} + \chi_{ik} + \chi_{jk}\text{]} \\
\]

(10)

The overall change in thermodynamic property due to process (i) (a, b, c) and (ii) would then be expressed by the relation

\[
X^E (X = V \text{ or } K_{\text{ijk}}) = \left\{ \begin{array}{l}
[x_i x_j V_j / \Sigma x_i V_i] (X_{ij} + x_j X_{12}) \\
\quad + [x_j x_k V_k / \Sigma x_i V_i] (X_{jk} + x_k X_{12}) \\
\quad + [x_i x_k V_k / \Sigma x_i V_i] (X_{ik} + x_k X_{12})
\end{array} \right. \\
\]

(14)
Since $V/V_i = \frac{3}{2}x^3$; where $3x^3$ (i = i or j) etc are the connectivity parameters defined by

$$3x^3 = \sum_{m=1}^{m} \beta m_{m} \delta_{m}^{*} \delta_{m}^{*} \delta_{m}^{*} \cdot 0.5 ... (15)$$

$\delta_{m}^{*}$ etc reflects explicitly the valency of the $m$th vertex in the molecular graph, and is related to the maximum valency $Z_m$, and number of hydrogen atoms $h_m$ attached to the $m$th vertex by

$$\delta_{m}^{*} = Z_m - h_m.$$ Equation (14), then reduces to Eq. (16)

$$X' = \frac{1}{x} \left( \frac{3}{2}x^3 \right) \left( \frac{x + x}{x + x} \right) \left( \frac{x + x}{x + x} \right) [X + X + X] + \frac{1}{x} \left( \frac{3}{2}x^3 \right) \left( \frac{x + x}{x + x} \right) \left( \frac{x + x}{x + x} \right) [X + X + X] + \frac{1}{x} \left( \frac{3}{2}x^3 \right) \left( \frac{x + x}{x + x} \right) \left( \frac{x + x}{x + x} \right) [X + X + X] + ... \quad(16)$$

Further, if it be assumed that $X = X = X$, then Eq. (16) can be expressed by Eq. (17) as

$$X' = \frac{1}{x} \left( \frac{3}{2}x^3 \right) \left( \frac{x + x}{x + x} \right) \left( \frac{x + x}{x + x} \right) [X + X + X] + \frac{1}{x} \left( \frac{3}{2}x^3 \right) \left( \frac{x + x}{x + x} \right) \left( \frac{x + x}{x + x} \right) [X + X + X] + \frac{1}{x} \left( \frac{3}{2}x^3 \right) \left( \frac{x + x}{x + x} \right) \left( \frac{x + x}{x + x} \right) [X + X + X] + ... \quad(17)$$

Equation (17) contains three unknown parameters (X, X, X) that were evaluated from the experimental $V'_{ik}$ and ($K_{ik}$) data of the (i+j+k) ternary mixtures at three compositions, and were then subsequently utilized to predict $X'_{ik}$ values at various values of $x_i$ and $x_j$. Such evaluated parameters along with the predicted $X'_{ik}$ ($X = V$ or $K$) values for the studied ternary mixtures are recorded in Tables 1 and 2, and are also compared with their corresponding experimental values.

Examination of Tables 1 and 2 reveals that the predicted $X'_{ik}$ ($X = V$ or $K$) values by Graph theory correlate well with the experimental values. Even in those cases where agreement between two values is not so good, the predicted values are of right order of magnitude. However, the theory fails to predict the sign of (i) $V'_{ik}$ values in the range $x_i \geq 0.63$ for D(i) + benzene + (i) or +p-xylene (k) ternary mixtures and (ii) ($K_{ik}$) values in the range $x_j \geq 0.71$ for D(i) + benzene (j) + p-xylene (k). This may be due to the presence of ternary i-j-k contacts which have not been presently considered.

$V'_{ik}$ and ($K_{ik}$) data for various (i+j+k) ternary mixtures were next analysed in terms of Flory's16,17 theory. According to Flory's theory16,17, $V'_{ik}$ for a ternary mixture is given by

$$V'_{ik} = V'_{ei} \sum \chi_i V'_{ik}$$

where

<table>
<thead>
<tr>
<th>Table 1—Comparison of the measured $V'<em>{ik}$ values for various ternary mixtures at 298.15 K with the corresponding values evaluated from (i) Graph theory; (ii) also recorded are the various $V'</em>{ik}$ values for the (i+j-k) parameters, standard deviation, and interaction energy values ($\chi_{ik}$) etc.</th>
<th>1.3 dioxolane (i) + benzene (j) + toluene(k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V'_{ik}$ (cm$^3$ mol$^{-1}$)</td>
<td>$x_i$</td>
</tr>
<tr>
<td>0.0507</td>
<td>0.6778</td>
</tr>
<tr>
<td>0.0967</td>
<td>0.6731</td>
</tr>
<tr>
<td>0.2449</td>
<td>0.2463</td>
</tr>
<tr>
<td>0.3198</td>
<td>0.2600</td>
</tr>
<tr>
<td>0.3723</td>
<td>0.2454</td>
</tr>
<tr>
<td>0.4195</td>
<td>0.2213</td>
</tr>
<tr>
<td>0.4613</td>
<td>0.3121</td>
</tr>
<tr>
<td>0.5272</td>
<td>0.3493</td>
</tr>
<tr>
<td>0.5917</td>
<td>0.1197</td>
</tr>
<tr>
<td>0.6443</td>
<td>0.2789</td>
</tr>
<tr>
<td>0.7803</td>
<td>0.0669</td>
</tr>
<tr>
<td>0.8219</td>
<td>0.0457</td>
</tr>
<tr>
<td>0.8923</td>
<td>0.0491</td>
</tr>
</tbody>
</table>

| 1.3 dioxolane (i) + benzene (j) + toluene(k) |
|---|---|
| $V'_{ik}$ (cm$^3$ mol$^{-1}$) | $x_i$ | $x_j$ | $x_k$ | Expst | Graph |
| 0.0397 | 0.7814 | 0.117 | 0.071 | 0.201 | 0.201 |
| 0.0599 | 0.5902 | 0.187 | 0.268 | 0.311 | 0.311 |
| 0.0981 | 0.7184 | 0.090 | 0.170 | 0.232 | 0.232 |
| 0.1264 | 0.3429 | 0.188 | 0.281 | 0.391 | 0.391 |
| 0.1631 | 0.1788 | 0.258 | 0.170 | 0.391 | 0.391 |
| 0.1953 | 0.2373 | 0.272 | 0.271 | 0.420 | 0.420 |
| 0.2355 | 0.5244 | 0.050 | 0.205 | 0.335 | 0.335 |
| 0.2960 | 0.4343 | 0.016 | 0.191 | 0.374 | 0.374 |
| 0.4157 | 0.2016 | 0.017 | 0.114 | 0.441 | 0.441 |
| 0.5627 | 0.3520 | 0.092 | 0.154 | 0.230 | 0.230 |
| 0.6792 | 0.1225 | 0.071 | -0.030 | 0.303 | 0.303 |
| 0.7386 | 0.1050 | 0.027 | -0.028 | 0.336 | 0.336 |
| 0.8172 | 0.0631 | 0.021 | -0.047 | 0.274 | 0.274 |

$V'_{ik} = -3.18 \cdot 10^{-5}; V'_{ik} = -2.00 \cdot 10^{-5}$; $V'_{ik} = 7.45 \cdot 10^{-5}$; $V'_{ik} = 0.002$; $\chi_{ik} = 0.530$; $\chi_{ik} = 0.666$; $\chi_{ik} = 1.426$

$V'_{ik} = -3.18 \cdot 10^{-5}; V'_{ik} = -2.00 \cdot 10^{-5}$; $V'_{ik} = 7.45 \cdot 10^{-5}$; $V'_{ik} = 0.002$; $\chi_{ik} = 0.530$; $\chi_{ik} = 0.666$; $\chi_{ik} = 1.426$

$V'_{ik} = -3.18 \cdot 10^{-5}; V'_{ik} = -2.00 \cdot 10^{-5}$; $V'_{ik} = 7.45 \cdot 10^{-5}$; $V'_{ik} = 0.002$; $\chi_{ik} = 0.530$; $\chi_{ik} = 0.666$; $\chi_{ik} = 1.426$

$V'_{ik} = -3.18 \cdot 10^{-5}; V'_{ik} = -2.00 \cdot 10^{-5}$; $V'_{ik} = 7.45 \cdot 10^{-5}$; $V'_{ik} = 0.002$; $\chi_{ik} = 0.530$; $\chi_{ik} = 0.666$; $\chi_{ik} = 1.426$
\[ \overline{V}_i^a = \overline{V}_i^{(0)}(4/3) - \overline{V}_i^{(0)} \] (19)
\[ \overline{V}_i = [\alpha_i T / (3 \alpha_i T + 3 + 1)] \] (20)
\[ T^* = N \overline{V}_i^{(0)}(\overline{V}_i^{(0)} - 1) \] (21)
\[ P^* = \sum_{i=1}^k \phi_i P_i^{*} - \sum_{i=1}^k \phi_i \theta_i \chi_{ij} \] (22)
\[ V_0 = \sum_i \phi_i V_i \] (23)
\[ \overline{T}_0 = [1 \{ (\overline{V}_0)^{1/3} - 1 \} / \overline{V}_0^{(0)}] \] (24)
\[ T = (T / P^*) \sum_i \phi_i P_i^{*} / T^* \] (25)

All terms have the same significance as described elsewhere.

Evaluation of \( V_{jk}^a \) according to this theory requires a knowledge of reduced temperature, \( T^* \), which in turn depends upon adjustable parameters \( \theta_i, \chi_{ij} \) etc. characteristic of \((i+j), (j+k)\) and \((i+k)\) sub-binary mixtures of \((i+j+k)\) ternary mixtures. These parameters were evaluated by employing \( H^E \)
experimental data (at \( x_i = 0.5 \)) of \((i+j),(j+k)\) and \((i+k)\) binary mixtures using Eq. (26)
\[ H^E = \sum_{i=1}^k P_i^{*} \sum_{i=1}^k V_i^{*} [\overline{V}_i^{(1)} - \overline{V}_0^{(1)}] + x_i V_i^{*} \theta_j \chi_{ij} \overline{V}_0^{(1)} \] (26)

The parameters of pure components were determined using isothermal compressibility \( (K_T) \) values reported in literature (25). \( K_T \) values for pure \( D(i) \) was calculated employing \( \Delta H^E \) values as suggested by Hildebrand (26). These parameters along with \( \theta_i, \chi_{ij} \) etc. were then utilized to predict \( V_{jk}^a \) values at various values of \( x_i \). Such \( V_{jk}^a \) values are recorded in Table 2 and are also compared with their corresponding experimental values.

According to Flory's theory, \( (K_T)_{jk}^a \) for ternary mixture is expressed by the relation
\[ (K_T)_{jk}^a = K_j - K_k \] (27)

The isentropic compressibility, \( K_s \), for \((i+j+k)\) mixture is determined using Eq. (28)
\[ K_s = \left[ K_T - T V_m \alpha_s^2 / C_{pm} \right] \] (28)

where
\[ K_T = \left[ (3 \overline{V}_0^2 m)(4 - 3 \overline{V}_m^{(1)}) / \overline{P}_m^{*(\overline{V}_m - 1)} \right] \] (29)
\[ \alpha_s = \left[ 3 (\overline{V}_0^{(1)} - 1) / T^*(4 - 3 \overline{V}_m^{(1)}) \right] \] (30)
\[ C_{pm} = (\partial H^E_{jk} / \partial T) + \sum_{i=1}^k x_i C_{pm}^* \] (32)

and all the terms have same significance as described elsewhere (17,18).

<table>
<thead>
<tr>
<th>1,3 dioxane (i) + benzene (j) + toluene (k)</th>
<th>Urm. (1)</th>
<th>Expdt (Graph)</th>
<th>Flory</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \chi_{12} )</td>
<td>0.0621</td>
<td>0.0481</td>
<td>1307.7</td>
</tr>
<tr>
<td>( \chi_{13} )</td>
<td>0.0333</td>
<td>0.1511</td>
<td>1309.2</td>
</tr>
<tr>
<td>( \chi_{23} )</td>
<td>0.0175</td>
<td>0.0635</td>
<td>1303.9</td>
</tr>
<tr>
<td>( \chi_{11} )</td>
<td>0.1756</td>
<td>0.1368</td>
<td>1308.6</td>
</tr>
<tr>
<td>( \chi_{22} )</td>
<td>0.2776</td>
<td>0.2139</td>
<td>1317.6</td>
</tr>
<tr>
<td>( \chi_{33} )</td>
<td>0.3042</td>
<td>0.4612</td>
<td>1322.6</td>
</tr>
<tr>
<td>( \chi_{21} )</td>
<td>0.3437</td>
<td>0.3509</td>
<td>1338.0</td>
</tr>
<tr>
<td>( \chi_{32} )</td>
<td>0.4064</td>
<td>0.3951</td>
<td>1352.5</td>
</tr>
<tr>
<td>( \chi_{31} )</td>
<td>0.4526</td>
<td>0.2831</td>
<td>1343.4</td>
</tr>
<tr>
<td>( \chi_{1} )</td>
<td>0.5096</td>
<td>0.1585</td>
<td>1326.6</td>
</tr>
<tr>
<td>( \chi_{2} )</td>
<td>0.6882</td>
<td>0.2193</td>
<td>1336.5</td>
</tr>
<tr>
<td>( \chi_{3} )</td>
<td>0.6063</td>
<td>0.1402</td>
<td>1314.1</td>
</tr>
<tr>
<td>( \chi_{4} )</td>
<td>0.8289</td>
<td>0.0758</td>
<td>1338.6</td>
</tr>
<tr>
<td>( \chi_{5} )</td>
<td>0.9049</td>
<td>0.0671</td>
<td>1377.3</td>
</tr>
</tbody>
</table>

Table 2—Comparison of the measured \((K_{sl})_{jk}^a \) values for the various ternary mixtures at 298.15 K with the corresponding values evaluated from graph. Flory theory: also recorded are the various \((K_{sl})_{jk}^a \) parameters, standard deviation, \((K_{sl})_{jk}^a \) interaction energies \((\chi_{ju}, \chi_{ju}^*, \chi_{ju}^* \text{ etc.})\) and \( \chi_{jk}^a \).
\( \frac{\partial H_{ik}^E}{\partial T} \) values for D(i) + benzene (j) or + toluene or + \( o\) - xylene and + \( p\)-xylene (k) ternary mixtures were calculated employing \( H_{ij}^{E,5,18} \) etc values for the (i+j), (j+k) and (i+k) binary mixtures. \( H_{ik}^E \) were taken equal to \( H_{ij}^{E} + H_{jk}^{E} + H_{ik}^{E} \). \( H_{ij}^{E} \) etc values at 308.15K were determined in the manner described elsewhere \(^{21}\). \( K_{ij}^{abcd} \) values for the corresponding ideal mixtures were determined using Eq. (28). \( a_{id} \) and \( C_{pm}^{id} \) were taken as the mole fraction averages of pure component. \( (K_{ijk}^{E})^{abcd} \) values calculated for the various (i+j+k) ternary mixtures are recorded in Table 2 and are also compared with their corresponding experimental values.

Examination of Tables 1 and 2 reveals that \((K_{ijk}^{E})^{abcd} \) values predicted from Flory theory made a reasonably good agreement with corresponding experimental values. However, \( V_{ijk}^{E} \) values calculated from Flory theory make only qualitative agreement with their experimental values. Flory theory fails to predict the sign of \( V_{ijk}^{E} \) values for D(i) + benzene (j) + toluene (k) ternary mixture.

The present analysis, thus, has shown that the Mooney-Huggins concept can be extended to evaluate molar excess volume and molar excess compressibility for the studied (i+j+k) ternary mixtures, and the predicted \( X_{ijk}^{E} (X = V \) or \( K_e \)) values by this approach compare better with their corresponding experimental values than the \( X_{ijk}^{E} \) values predicted by Flory theory.

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References