Topological investigations of binary and ternary mixtures containing cyclic ether: Excess isentropic compressibilities

Vinod K. Sharma*, Romi & Satish Kumar
Department of Chemistry, Maharshi Dayanand University Rohtak 124 001, India

Received 31 January 2003

Speed of sound, \( U \), of 1,3-dioxolane (i) + toluene (j) or + o- or + p-xylene (j) binary and 1,3-dioxolane (i) + toluene (j) + o- or + p-xylene(k) ternary mixtures have been measured over the whole mole fraction range at 298.15 K. Excess isentropic compressibility, \( K_{SE} \) values have been calculated employing density, \( \rho_j \) and \( \rho_{jk} \) speed of sound values of the binary and ternary mixtures. The \( K_{SE} \) values for the binary and ternary mixtures have also been evaluated by employing graph theory. It has been observed that \( K_{SE} \) values predicted by graph theoretical approach compare reasonably well with the \( K_{SE} \) values determined from experimental data.

Ever since the suggestion that constitutional formula of the chemist is a special kind of graph, a very good correlation has been observed between topological index \( I \) of a molecule and its physico-chemical properties. The concept of molecular parameters of third degrees of the constituents of binary as well as ternary mixtures have been successfully utilized to evaluate: (i) molar excess volumes and molar excess enthalpies of binary and ternary mixtures of non-electrolytes; (ii) molar excess free energy date of binary mixtures; and (iii) states of components in pure and mixtures and their extent of interactions in the mixtures.

In the present work an attempt has been made to evaluate molar excess compressibilities of binary and ternary mixtures by extending Moelwyn Huggins concept of interactions between the molecular surfaces of the components of binary mixtures.

Materials and Methods

1,3-dioxolane (D) [Fluka], benzene, toluene, and o- or p-xyles (AR grade) were purified by standard methods. The purities of the purified compounds were checked by measuring their density at 298.15 ± 0.01 K which agreed to within ± 0.05 kg m\(^{-3}\) with the corresponding literature values.

Speed of sound at frequency 2 MHz for binary and ternary were measured using a quartz crystal ultrasonic interferometer (Mittal Enterprises, New Delhi, India). The measuring cell was a specially designed cell and temperature was maintained by circulating water from thermostat controlled at (298 ± 0.01) K. These values were accurate to 0 ± 0.05 per cent.

Results

Speed of sound, \( U \), data of D(i) + toluene or + o- or + p-xylene binary and U, \( \rho_j \) of D(i) + toluene (j) + o-xylene or + p-xylene (k) ternary mixtures for the whole mole fraction range are reported in Tables 1 and 2. The isentropic compressibility, \( K_s \) values were estimated from experimentally measured speed of sound \( U \) and density of mixtures, \( \rho_j \) values using Eq. (1)

\[
K_s = \left( \rho_j U_j^2 \right)^{-1}
\]

The density, \( \rho_j \) and \( \rho_{jk} \) of binary and ternary mixtures were determined from their experimental \( V^E \) data of (i+j) and (i+j+k) mixtures using the relation

\[
V^E = \sum_{i=1}^{i} x_i M_i (\rho_j)^{-1} - \sum_{i=1}^{i} (x_i M_i) (\rho_i)^{-1}
\]

where \( x_i, M_i \) etc are the mole fraction and molar mass of component (i) of the mixture.

Excess isentropic compressibilities, \( K_{SE} \) were calculated from Eqs (3) and (4)

\[
K_{SE} = K_s - \sum_{i=1}^{i} \phi_i (K_{Sh})
\]

\[
K_{SE} = K_s - \sum_{i=1}^{i} \phi_i (K_{Sh})
\]
where \( \phi_i \) and \( (K_S^i) \) are the volume fraction and isentropic compressibility of i in the \((i+j)\) binary mixtures. Such \( K_S \) and \( K^{E}_{SE} \) values obtained from Eqs 3 and 4 for the studied mixtures are recorded in Tables 1 and 2. These \( K^{E}_{SE} \) values for binary mixtures were fitted to Eq. (5).

\[
K^{E}_{SE} = \sum_{n=0}^{2} \left[ \sum_{i=0}^{n} K^{(n)}_{ij} (x_i - x_j)^n \right] + \sum_{n=0}^{2} \left[ \sum_{i=0}^{n} K^{(n)}_{ik} (x_i - x_k)^n \right] + \sum_{n=0}^{2} \left[ \sum_{i=0}^{n} K^{(n)}_{jk} (x_j - x_k)^n \right] + \sum_{n=0}^{2} \left[ \sum_{i=0}^{n} K^{(n)}_{ik} (x_i - x_k)^n \right]
\]

where \( x_i \) is the mole fraction of component i, \( K^{(n)}_{ij} \) (\( n = 0 - 2 \)) etc are the adjustable parameters of \((i+j)\) mixtures and were calculated using the method of least squares. These parameters are recorded along with standard deviation \( \sigma \) of \( K^{(n)}_{ij} \) as defined by

\[
\sigma \left( K^{E}_{SE} \right) = \left\{ \sum (K^{E}_{SE} \text{ (exp))} - (K^{E}_{SE} \text{ (calcd)}})^2 / (m-n) \right\\
\]

Excess compressibility for ternary \((i+j+k)\) mixtures were expressed as

\[
(K^{E}_{SE})_{ijk} = \sum_{n=0}^{2} \left[ \sum_{i=0}^{n} K^{(n)}_{ijk} (x_i - x_k)^n \right] + \sum_{n=0}^{2} \left[ \sum_{i=0}^{n} K^{(n)}_{ijk} (x_j - x_k)^n \right] + \sum_{n=0}^{2} \left[ \sum_{i=0}^{n} K^{(n)}_{ijk} (x_i - x_k)^n \right] + \sum_{n=0}^{2} \left[ \sum_{i=0}^{n} K^{(n)}_{ijk} (x_i - x_k)^n \right] + \sum_{n=0}^{2} \left[ \sum_{i=0}^{n} K^{(n)}_{ijk} (x_i - x_k)^n \right]
\]

where \( (K^{E}_{SE})_{ijk} \) \( (n = 0-2) \) etc. are parameters characteristics of \((i+j), (j+k)\) and \((i+k)\) binary mixtures and have been taken from literature \(24\). \( K^{E}_{SE} \) \((n = 0-2)\)

<table>
<thead>
<tr>
<th>( x_i )</th>
<th>( U_m(\text{ms}^{-1}) )</th>
<th>( (K_S^i)_m(\text{TPa}^{-1}) )</th>
<th>( (K^{E}_{SE})_m(\text{TPa}^{-1}) )</th>
<th>( x_i )</th>
<th>( U_m(\text{ms}^{-1}) )</th>
<th>( (K_S^i)_m(\text{TPa}^{-1}) )</th>
<th>( (K^{E}_{SE})_m(\text{TPa}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0687</td>
<td>1311</td>
<td>677.0</td>
<td>-3.2</td>
<td>0.4978</td>
<td>1342</td>
<td>591.4</td>
<td>-3.1</td>
</tr>
<tr>
<td>0.1281</td>
<td>1312</td>
<td>667.8</td>
<td>-5.8</td>
<td>0.5390</td>
<td>1341</td>
<td>587.4</td>
<td>-3.2</td>
</tr>
<tr>
<td>0.1964</td>
<td>1314</td>
<td>657.2</td>
<td>-8.6</td>
<td>0.5851</td>
<td>1341</td>
<td>582.7</td>
<td>-3.3</td>
</tr>
<tr>
<td>0.2461</td>
<td>1318</td>
<td>649.4</td>
<td>-10.4</td>
<td>0.6382</td>
<td>1340</td>
<td>577.1</td>
<td>-3.2</td>
</tr>
<tr>
<td>0.2933</td>
<td>1320</td>
<td>641.9</td>
<td>-12.0</td>
<td>0.7148</td>
<td>1340</td>
<td>568.6</td>
<td>-3.0</td>
</tr>
<tr>
<td>0.3395</td>
<td>1322</td>
<td>634.7</td>
<td>-13.3</td>
<td>0.7988</td>
<td>1339</td>
<td>558.5</td>
<td>-2.5</td>
</tr>
<tr>
<td>0.3951</td>
<td>1325</td>
<td>625.9</td>
<td>-14.5</td>
<td>0.8721</td>
<td>1339</td>
<td>548.9</td>
<td>-1.8</td>
</tr>
<tr>
<td>0.4624</td>
<td>1327</td>
<td>615.4</td>
<td>-15.5</td>
<td>0.9416</td>
<td>1338</td>
<td>539.0</td>
<td>-0.9</td>
</tr>
<tr>
<td>0.5388</td>
<td>1330</td>
<td>590.9</td>
<td>-15.3</td>
<td>0.6845</td>
<td>1332</td>
<td>-14.3</td>
<td>0.4999</td>
</tr>
<tr>
<td>0.6204</td>
<td>1333</td>
<td>580.9</td>
<td>-14.3</td>
<td>0.1028</td>
<td>1330</td>
<td>660.4</td>
<td>-5.1</td>
</tr>
<tr>
<td>0.6845</td>
<td>1333</td>
<td>586.6</td>
<td>-12.1</td>
<td>0.1913</td>
<td>1330</td>
<td>653.2</td>
<td>-8.4</td>
</tr>
<tr>
<td>0.7639</td>
<td>1335</td>
<td>578.7</td>
<td>-9.4</td>
<td>0.2456</td>
<td>1321</td>
<td>646.1</td>
<td>-10.0</td>
</tr>
<tr>
<td>0.8325</td>
<td>1336</td>
<td>548.0</td>
<td>-6.4</td>
<td>0.2950</td>
<td>1323</td>
<td>639.5</td>
<td>-11.2</td>
</tr>
<tr>
<td>0.8931</td>
<td>1337</td>
<td>536.5</td>
<td>-2.5</td>
<td>0.3469</td>
<td>1324</td>
<td>632.7</td>
<td>-12.2</td>
</tr>
<tr>
<td>0.9621</td>
<td>1337</td>
<td>-63.1</td>
<td>(K^{E}<em>{SE})</em>{ij} = -12.4; (K^{E}<em>{SE})</em>{ik} = -5.4; (K^{E}<em>{SE})</em>{jk} = -8.2; \sigma (K^{E}_{SE})_m = 0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.3-dioxolane (i) + p-xylene (j)</td>
<td>0.0389</td>
<td>1345</td>
<td>628.4</td>
<td>-0.3</td>
<td>0.4724</td>
<td>1327</td>
<td>615.6</td>
</tr>
<tr>
<td>0.0952</td>
<td>1344</td>
<td>624.6</td>
<td>-0.7</td>
<td>0.5358</td>
<td>1328</td>
<td>606.7</td>
<td>-13.9</td>
</tr>
<tr>
<td>0.1584</td>
<td>1344</td>
<td>620.1</td>
<td>-1.1</td>
<td>0.6108</td>
<td>1330</td>
<td>595.8</td>
<td>-13.6</td>
</tr>
<tr>
<td>0.2103</td>
<td>1344</td>
<td>616.2</td>
<td>-1.5</td>
<td>0.6859</td>
<td>1332</td>
<td>584.4</td>
<td>-12.8</td>
</tr>
<tr>
<td>0.2906</td>
<td>1343</td>
<td>609.8</td>
<td>-2.1</td>
<td>0.7711</td>
<td>1330</td>
<td>570.9</td>
<td>-10.9</td>
</tr>
<tr>
<td>0.3494</td>
<td>1343</td>
<td>604.9</td>
<td>-2.4</td>
<td>0.8639</td>
<td>1335</td>
<td>555.2</td>
<td>-7.6</td>
</tr>
<tr>
<td>0.3926</td>
<td>1342</td>
<td>601.1</td>
<td>-2.7</td>
<td>0.9592</td>
<td>1337</td>
<td>537.8</td>
<td>-2.7</td>
</tr>
<tr>
<td>0.4311</td>
<td>1342</td>
<td>597.7</td>
<td>-2.9</td>
<td>(K^{E}<em>{SE})</em>{ij} = -55.4; (K^{E}<em>{SE})</em>{ik} = -7.1; (K^{E}<em>{SE})</em>{jk} = -8.2; \sigma (K^{E}_{SE})_m = 0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
etc. are parameters characteristics of \((i+j+k)\) ternary mixtures. These parameters were evaluated by fitting \((K_{S}^{E})_{ijk}\) data to the expression (7)

\[
(K_{S}^{E})_{ijk} - x_{j}x_{k} \left[ \sum_{n=0}^{\infty} \left( K_{S}^{E} \right)_{ijn} (x_{i}-x_{j})^{n} \right] - x_{i}x_{k} \left[ \sum_{n=0}^{\infty} \left( K_{S}^{E} \right)_{ikn} (x_{i}-x_{k})^{n} \right] \\
\]

\[
= x_{j}x_{k} \left[ \sum_{n=0}^{\infty} \left( K_{S}^{E} \right)_{ijn} (x_{j}-x_{k})^{n} \right] \sum_{n=0}^{\infty} \left( K_{S}^{E} \right)_{ikn} (x_{i}-x_{k})^{n} 
\]

by least squares method. Such parameters along with standard deviation, \(\sigma(K_{S}^{E})_{ijk}\), are recorded in Table 2.

### Discussion

We are unaware of any \(K_{S}^{E}\) data for these mixtures with which to compare our results. However, there is good agreement between the experimentally observed and literature values of speed of sound for pure liquids. toluene: \(1304.5\) \(\text{ms}^{-1}\) \((1304.0)^{25}\), \(\alpha\)-xylene: \(1344.9\) \(\text{ms}^{-1}\) \((1345.0)^{26}\), \(p\)-xylene: \(1310.1\) \(\text{ms}^{-1}\) \((1309.6)^{27}\).

\(K_{S}^{E}\) values for the studied \((i+j)\) mixtures are negative over the entire range of composition and for an equimolar mixture vary in the order: \(\alpha\)-xylene > \(p\)-xylene > toluene.

#### Conceptual aspect of graph theory and results

According to mathematical discipline of graph theory, if the atoms in a structural formula of a molecule are represented by letters and bonds joining them by lines then the resulting graph describes the totality of information contained in that molecule\(^{27,29}\). Consequently if \(\delta_{m}, \delta_{n}\) etc. represent the degrees of \(m\) and \(n\) etc. vertices of the graph of a molecule, then connectivity parameters of third degree, \(3\xi\) is defined by\(^{30}\)

\[
3\xi = \sum_{m<n<0} (\delta_{m} > \delta_{n}> \delta_{p})^{0.5} 
\]

where \(\delta_{m}\) etc. reflects explicitly\(^{30}\) the valency of \(m\)-th vertex in molecular graph of \(i\) in forming bonds and is related to maximum valency, \(Z_{m}\) and number of hydrogen atoms, \(h_{m}\) attached to \(m\)-th etc vertex by relation\(^{31}\)

\[
\delta_{m} = Z_{m} - h_{m} 
\]

Further Kier\(^{32}\) has suggested that information regarding effect of branching in the molecules can be obtained by evaluating \(3\xi\) of molecules.

Since the addition of \(i\) to \(j\) would cause structural changes in their topology. So analysis of \(V^{E}\) and \(H^{E}\) in terms of graph theory reflect changes in the topologies of \(i\) or \(j\) in \((i+j)\) mixtures. Molar excess volumes, \(V^{E}\) and molar excess enthalpies, \(H^{E}\) studies by graph

### Table 2—Comparison of the excess isentropic compressibility \(K_{S}^{E}\) for the various \((i+j)\) mixtures as function of \(x_{i}\), mole fraction of component \(i\) at 298.15K with values evaluated from Graph theory; also included are the interaction energy parameter \(\chi_{ij}\) etc.

<table>
<thead>
<tr>
<th>Property</th>
<th>(x_{i})</th>
<th>(0.1)</th>
<th>(0.2)</th>
<th>(0.3)</th>
<th>(0.4)</th>
<th>(0.5)</th>
<th>(0.6)</th>
<th>(0.7)</th>
<th>(0.8)</th>
<th>(0.9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K_{S}^{E}) (exptl)</td>
<td>l,3-dioxolane (i) + toluene (j)</td>
<td>-4.6</td>
<td>-8.8</td>
<td>-12.1</td>
<td>-14.6</td>
<td>-15.8</td>
<td>-15.6</td>
<td>-13.9</td>
<td>-10.7</td>
<td>-6.0</td>
</tr>
<tr>
<td>(K_{S}^{E}) (Graph)</td>
<td>l,3-dioxolane (i) + toluene (j)</td>
<td>-4.8</td>
<td>-8.9</td>
<td>-12.3</td>
<td>-15.6</td>
<td>-14.1</td>
<td>-10.9</td>
<td>-6.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\chi_{ij})</td>
<td>l,3-dioxolane (i) + toluene (j)</td>
<td>-113.636; (\chi_{ij} = 64.304)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| \(K_{S}^{E}\) (exptl) | l,3-dioxolane (i) + p-xylene (j) | -4.9 | -8.7 | -11.1 | -13.0 | -13.8 | -13.7 | -12.5 | -9.9 | -5.2 |
| \(K_{S}^{E}\) (Graph) | l,3-dioxolane (i) + p-xylene (j) | -4.5 | -8.3 | -11.2 | -13.5 | -11.9 | -9.2 | -5.2 |
| \(\chi_{ij}\) | l,3-dioxolane (i) + p-xylene (j) | -138.636; \(\chi_{ij} = 91.458\) |

| \(K_{S}^{E}\) (exptl) | l,3-dioxolane (i) + o-xylene (j) | -0.7 | -1.4 | -2.1 | -2.6 | -3.2 | -3.2 | -3.0 | -2.4 | -1.4 |
| \(K_{S}^{E}\) (Graph) | l,3-dioxolane (i) + o-xylene (j) | -0.5 | -1.3 | -2.1 | -3.2 | -2.9 | -2.3 | -1.4 |

\(\chi_{ij}\) etc. are in TPa\(^{-1}\)
theory for the D(i) + benzene, or + toluene (j) or + o-
or + p-xylene (j) binary mixtures have revealed\(^1\) that
(i) D(j) and tolune or o-, or –p-xylene exist as
monomers in their pure state and these (i+j) mixtures
are characterized by specific interactions between
delocalized \(\pi\)-electrons of aromatic ring of aromatic
hydrocarbons and \(\pi\)-electrons of oxygen atom of D(i)
in cyclic ether. Further these mixtures formation in-
volve the processes (I) establishment of unlike contact
between (i) and (j), (II) monomers of i and j then un-
dergoes specific interactions to form i-j molecular
entity. Consequently, if \(\chi_{ij}\) are molar compressibility
interaction and molar specific interaction parameters
for i-j contact, then change in molar isentropic compressibility
due to processes (I) – (II) would be given by\(^{21,33,34}\).

\[
\Delta X_1 (X = K_S) = \left[ (x_i x_j V_j) / \Sigma x_i V_i \right] \quad \ldots \quad (10)
\]

and

\[
\Delta X_2 (X = K_S) = x_i x_j^2 V_j \chi_{12} / \Sigma x_i V_i \quad \ldots \quad (11)
\]

where \(V_i\) is the molar volume of component i.

The overall change in thermodynamic property, \(X^E\)
would be given by

\[
X^E = \Sigma \Delta X_i
\]

\[
K_S^E = [x_i x_j V_i / \Sigma x_i V_i] [\chi_{ij} + x_i \chi_{12}] \quad \ldots \quad (12)
\]

Since \(V_i / V_j = (\chi_j \chi_j) / \chi_j^j\),

So Eq. (12) reduces to

\[
K_S^E = [x_i x_j (\chi_j \chi_j) / (\chi_j + x_i (\chi_j \chi_j))] [\chi_{ij} + x_i \chi_{12}] \quad \ldots \quad (13)
\]

Equation (13) contains two unknown parameters \(\chi_{ij}\)
and \(\chi_{12}\). These parameters were determined from \(K_S^E\)
data of studied mixtures at \(x_j = 0.4\) and \(x_j = 0.5\) and
were subsequently utilized to predict \(K_S^E\) values at
various values of \(x_i\). Such \(K_S^E\) values along with \(\chi_{ij}\), \(\chi_{12}\)
parameters are recorded in Table 2.

Further in toluene (i) + o-xylene (j) or p-xylene (j),
if toluene (i) and o-xylene or p-xylene undergo spec-
cific interactions, then \(K_S^E\) data of these mixtures
would also be expressible by relation

\[
X^E = [x_i x_k (\chi_j \chi_j) / (\chi_j + x_k (\chi_j \chi_j))] [\chi_{jk} + x_k \chi_{12}] \quad \ldots \quad (14)
\]

The basic arguments in deriving eqns (13) and (14)
are justified as \(K_S^E\) data of these binary mixtures are
reproduced\(^1\) by employing \(\chi_{ij}, \chi_{jk}\) and \(\chi_{12}\) parameters
(Table 3).

If a third component like o-xylene or p-xylene (k)
is added to D(i) + toluene (j) binary mixture; then D(i)
Table 3—Comparison of the measured \((K_S^E)_{jk}\) values for the tern-
ary mixtures at 298.15 K with the corresponding values evaluated
from Graph Theory; also recorded are the various \((K_S^E)_{jk}\) \((n = 0-2)\) parameters, standard deviation, \(\sigma(K_S^E)_{jk}\) interaction energies \((\chi_{ijk}^E, \chi_{ik}^E, \chi_{jk}^E)\) etc.

<table>
<thead>
<tr>
<th>(x_i)</th>
<th>(x_j)</th>
<th>(x_k)</th>
<th>(U_{\text{ms}})</th>
<th>(\chi_{ijk}^E)</th>
<th>Graph</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0509</td>
<td>0.8112</td>
<td>0.1367</td>
<td>1214</td>
<td>-2.4</td>
<td>-3.4</td>
</tr>
<tr>
<td>0.0864</td>
<td>0.7344</td>
<td>0.1664</td>
<td>1317</td>
<td>-3.9</td>
<td>-5.5</td>
</tr>
<tr>
<td>0.0943</td>
<td>0.6822</td>
<td>0.1951</td>
<td>1320</td>
<td>-4.4</td>
<td>-5.8</td>
</tr>
<tr>
<td>0.1270</td>
<td>0.3201</td>
<td>0.5547</td>
<td>1335</td>
<td>-5.5</td>
<td>-6.8</td>
</tr>
<tr>
<td>0.2594</td>
<td>0.5547</td>
<td>0.1664</td>
<td>1321</td>
<td>-6.3</td>
<td>-11.4</td>
</tr>
<tr>
<td>0.3116</td>
<td>0.4510</td>
<td>0.2996</td>
<td>1299</td>
<td>-10.0</td>
<td>-12.7</td>
</tr>
<tr>
<td>0.3628</td>
<td>0.3891</td>
<td>0.1367</td>
<td>1333</td>
<td>-12.0</td>
<td>-13.4</td>
</tr>
<tr>
<td>0.4419</td>
<td>0.3126</td>
<td>0.1664</td>
<td>1337</td>
<td>-13.9</td>
<td>-13.9</td>
</tr>
<tr>
<td>0.4966</td>
<td>0.2996</td>
<td>0.1951</td>
<td>1335</td>
<td>-13.3</td>
<td>-13.3</td>
</tr>
<tr>
<td>0.5734</td>
<td>0.2102</td>
<td>0.1664</td>
<td>1339</td>
<td>-13.3</td>
<td>-13.3</td>
</tr>
<tr>
<td>0.6428</td>
<td>0.1987</td>
<td>0.1664</td>
<td>1338</td>
<td>-12.1</td>
<td>-11.3</td>
</tr>
<tr>
<td>0.7966</td>
<td>0.1192</td>
<td>0.1664</td>
<td>1339</td>
<td>-9.1</td>
<td>-11.8</td>
</tr>
<tr>
<td>0.7681</td>
<td>0.1286</td>
<td>0.1664</td>
<td>1338</td>
<td>-9.0</td>
<td>-8.2</td>
</tr>
<tr>
<td>0.8352</td>
<td>0.0891</td>
<td>0.1664</td>
<td>1337</td>
<td>-6.7</td>
<td>-6.1</td>
</tr>
</tbody>
</table>

\((K_S^E)_{jk}\) values in TPa\(^{-1}\), \(\chi_{ijk}^E\) etc. in TPa\(^{-1}\)
+ + toluene (j) or + o- or + p-xylene (k) ternary mixtures formation may be assumed to involve, (l) 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. If \( \chi'_{ij} \), \( \chi'_{jk} \) and \( \chi'_{ik} \) are the molar compressibility parameter (of unlike i-j, j-k and and i-k contact), then change in thermodynamic property \( K_{E} \) due to processes (II) [(a), (b) and (c)] would be expressible32-34 by Eq. (15)

\[
A \Delta X_{1} (X = K_{s}) = x_{i} \chi'_{ij} S_{j} + \chi'_{jk} S_{k} + x_{k} \chi'_{ik} S_{i} \quad \ldots \quad (15)
\]

where \( S_{i} \) etc. are defined21 by

\[
S_{i} = x_{i} V_{i} / \Sigma x_{i} V_{i} \quad \ldots \quad (16)
\]

so that

\[
A \Delta X_{1} = [(x_{i} x_{j} V_{j}) / \Sigma x_{i} V_{i}] \{ \chi'_{ij} + \chi'_{jk} + \chi'_{ik} \} \quad \ldots \quad (17)
\]

Further if \( \chi_{12} \), \( \chi_{12}' \) and \( \chi_{12}'' \) are the molar specific interaction parameters for i-j, j-k and i-k molecular entities, then change in molar isentropic compressibility due to processes (II) would be given34 by

\[
A \Delta X_{2} = x_{i} x_{j}^{2} V_{j} \chi_{12} \Sigma x_{i} V_{i} \quad \ldots \quad (18)
\]

\[
A \Delta X_{3} = x_{j} x_{k}^{2} V_{k} \chi_{12}' \Sigma x_{j} V_{j} \quad \ldots \quad (19)
\]

\[
A \Delta X_{4} = x_{k} x_{i}^{2} V_{i} \chi_{12} '' \Sigma x_{k} V_{k} \quad \ldots \quad (20)
\]

The overall change in thermodynamic property due to processes (i) (a, b, c) and (ii) would then be expressed by relation (21):

\[
A \Delta X_{E} (X = K_{s}) = \left( \begin{array}{c}
[x_{i} x_{j} V_{j} / \Sigma x_{i} V_{i}] [\chi'_{ij} + x_{j} \chi_{12}'] \\
[x_{j} x_{k} V_{k} / \Sigma x_{j} V_{j}] [\chi'_{jk} + x_{k} \chi_{12}''] \\
[x_{k} x_{i} V_{i} / \Sigma x_{k} V_{k}] [\chi'_{ik} + x_{i} \chi_{12}''']
\end{array} \right) \quad \ldots \quad (21)
\]

since \( V_{j} V_{i} = \beta_{j} / \beta_{i} \).

Equation (21), reduces to

\[
X_{E} = \left[ (x_{i} x_{j}^{3} + x_{j} x_{i}^{3}) / (x_{i} x_{j}^{3} + x_{j} x_{i}^{3}) \right] [\chi_{ij} + x_{j} \chi_{12}'] + \left[ (x_{j} x_{k}^{3} + x_{k} x_{j}^{3}) / (x_{j} x_{k}^{3} + x_{k} x_{j}^{3}) \right] [\chi'_{jk} + x_{k} \chi_{12}''] + \left[ (x_{k} x_{i}^{3} + x_{i} x_{k}^{3}) / (x_{k} x_{i}^{3} + x_{i} x_{k}^{3}) \right] [\chi'_{ik} + x_{i} \chi_{12}'''] \quad \ldots \quad (22)
\]

Further, if it be assumed that \( \chi'_{ij} = \chi_{12}' = \chi'_{ij}' \), \( \chi'_{jk} = \chi''_{jk} \); \( \chi'_{ik} = \chi''_{ik} \) and \( \chi''_{ik} = \chi''_{ik} \) then Eq. (21) can be expressed by Eq. (22)

\[
X_{E} = \left[ (x_{i} x_{j}^{3} x_{j}^{3}) / (x_{i} x_{j}^{3} + x_{j} x_{i}^{3}) \right] [1 + x_{j} \chi_{12}'] + \left[ (x_{j} x_{k}^{3} x_{k}^{3}) / (x_{j} x_{k}^{3} + x_{k} x_{j}^{3}) \right] [1 + x_{k} \chi_{12}''] + \left[ (x_{k} x_{i}^{3} x_{i}^{3}) / (x_{k} x_{i}^{3} + x_{i} x_{k}^{3}) \right] [1 + x_{i} \chi_{12}'''] \quad \ldots \quad (22)
\]

Equation (22) contains three unknown parameters \( \chi'_{ij}, \chi'_{jk}, \chi'_{ik} \) that were evaluated from experimental \( (K_{E})_{ijk} \) data of the (i+j+k) ternary mixtures at three compositions and were then subsequently utilized to predict \( (K_{E})_{ijk} \) values at various values of \( x_{i} \) and \( x_{j} \). Such evaluated parameters along with predicted \( (K_{E})_{ijk} \) values for the studied ternary mixtures are recorded in Table 2 and are also compared with their corresponding experimental values.

Examination of Table 1 and Table 2 reveals the predicted and \( (K_{E})_{ijk} \) values by Graph theory compare 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.

**Acknowledgement**

The authors express their thanks to the Head, Department of Chemistry and authorities of Maharsi Dayanand University, Rohtak for providing research facilities.

**References**

3. Cayley A, Phil Mag, 67 (1874) 444.