# Topological and thermodynamic investigations of binary mixtures: Molar excess volumes, molar excess enthalpies and isentropic compressibility changes of mixing

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## ARTICLE INFO

## ABSTRACT

Molar excess volumes, $V^E$, molar excess enthalpies, $H^E$, and speeds of sound, $u$, of $o$-toluidine ($i$) + cyclohexane or $n$-hexane or $n$-heptane ($j$) binary mixtures have been determined over entire range of composition at 308.15 K. Speeds of sound data have been utilized to predict isentropic compressibility changes of mixing, $\kappa_S^E$ of ($i+j$) mixtures. The observed $V^E$, $H^E$ and $\kappa_S^E$ data have been analyzed in terms of Graph theory. The analysis of $V^E$ data by Graph theory reveals that $o$-toluidine exists as an associated molecular entity and ($i+j$) mixtures contain 1:1 molecular complex. It has been observed that $V^E$, $H^E$ and $\kappa_S^E$ values calculated by Graph theory compare well with their corresponding experimental values. The observed data have also been analyzed in term of Flory theory.

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## 1. Introduction

Determination of the effects of mixing on thermodynamic properties is of importance in chemical engineering. Moreover, since these effects arise through their molecular interactions, knowledge of these interactions is essential for the study of thermodynamics of solutions. Molecular structure and molecular interactions play important role in determining the bulk properties of liquids [1]. Molecular structure of a compound can be viewed as a molecular graph, where atoms are represented by dots and bonds joining them are represented by lines. The topology of the molecule then describes the total information contained in that molecule [2–4]. Singh and Sharma et al. [5–10] have employed Graph theory (which involves topology of the constituents of the mixture) to evaluate molar excess volumes, $V^E$, molar excess enthalpies, $H^E$ and isentropic compressibility changes of mixing, $\kappa_S^E$ of binary and ternary mixtures. In recent study [11], Graph theory has been successfully utilized to evaluate molar excess volumes, $V^E$ and molar excess enthalpies, $H^E$ of $o$-toluidine ($i$) + aromatic hydrocarbons ($j$) binary mixtures. It would be of interest to see how (1) the replacement

of aromatic hydrocarbons by $n$-alkanes or cycloalkane influence the nature of interactions between $o$-toluidine and $n$-alkanes or cycloalkane in their binary mixtures and (2) Graph theory describes the $V^E$, $H^E$ and $\kappa_S^E$ data of the studied binary mixtures. These considerations prompted us to measure molar excess volumes, $V^E$, molar excess enthalpies, $H^E$ and speeds of sound, $u$, of $o$-toluidine ($i$) + $n$-hexane or $n$-heptane or cyclohexane ($j$) binary mixtures.

## 2. Experimental

$o$-Toluidine (OT) (Fluka), cyclohexane (AR Grade), $n$-hexane (AR Grade), $n$-heptane (AR grade) were purified by standard methods [12]. The purities of the purified samples were checked by measuring their densities (recorded in Table 1) at (298.15 ± 0.01 K) and these agreed to be within ±5 × 10$^{-3}$ kg m$^{-3}$ of their corresponding literature values [12].

Molar excess volumes, $V^E$ for binary mixtures were measured by means of a dilatometer as has been described elsewhere [13]. The change in liquid level in the dilatometer was measured with a cathetometer that could read to within ±0.001 cm. The uncertainty in the measured $V^E$ values is ±0.5%.

Molar excess enthalpies, $H^E$ for binary mixtures were measured by two-drop calorimeter (model, 4600) supplied by the Calorimeter Sciences Corporation (CSC), USA, in a manner as described

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**Table 1**
Comparison of densities, $\rho$, and speeds of sound, $u$, of pure liquids with their literature values at 298.15 K

| Liquid | $\rho$ (kg m$^{-3}$) | | $u$ (m s$^{-1}$) | |
|---|---|---|---|---|
| | Experimental | Literature | Experimental | Literature |
| o-Toluidine | 994.28 | 994.30 [11] | 1603[a] | – |
| Cyclohexane | 773.94 | 773.89 [11] | 1255 | 1254.4 [15] |
| n-Hexane | 654.82 | 654.84 [11] | 1079 | 1078 [15] |
| n-Heptane | 679.49 | 679.46 [11] | 1088 | 1087.6 [15] |

[a] Value at 308.15 K.

elsewhere [11] and the uncertainties in the measured $H^E$ values are ±1%.

Speeds of sound for various binary mixtures were measured using a variable path interferometer (Model-M 84, Mittal Enterprises, New Delhi, India). The measuring cell was a specially designed double-walled cell in which water was circulated to maintain the temperature at $308.15 \pm 0.01$ K. The speeds of sound values for the purified liquids at $(298.15 \pm 0.01$ K) (recorded in Table 1) compare well with their corresponding literature values [14,15]. The uncertainty in the measured speeds of sound value is $\pm 1$ m s$^{-1}$.

## 3. Results

The experimental molar excess volumes, $V^E$, molar excess enthalpies, $H^E$ and speeds of sound $u$, data of binary OT ($i$) + cyclohexane or $n$-hexane or $n$-heptane ($j$) mixtures as a function of composition at 308.15 K are recorded in Tables 2–4 (plotted in Figs. 1 and 2). The isentropic compressibilities, $\kappa_S$, values for binary mixtures were calculated using the following equation:

$$\kappa_S = \frac{1}{\rho_{ij} u^2} \tag{1}$$

**Table 2**
Measured molar excess volumes, $V^E$ data for the various ($i+j$) mixtures as a function of mole fraction, $x_i$, of component ($i$) at 308.15 K

| $x_i$ | $V^E$ (cm$^3$ mol$^{-1}$) | $x_i$ | $V^E$ (cm$^3$ mol$^{-1}$) |
|---|---|---|---|
| o-Toluidine ($i$) + cyclohexane ($j$)[a] | | | |
| 0.0768 | 0.241 | 0.4506 | 0.568 |
| 0.1415 | 0.387 | 0.5225 | 0.529 |
| 0.1925 | 0.470 | 0.6103 | 0.457 |
| 0.2442 | 0.529 | 0.6875 | 0.379 |
| 0.2901 | 0.562 | 0.7513 | 0.307 |
| 0.3415 | 0.581 | 0.8224 | 0.222 |
| 0.3981 | 0.582 | 0.9119 | 0.111 |
| o-Toluidine ($i$) + n-hexane ($j$)[b] | | | |
| 0.0712 | −0.048 | 0.4903 | −0.338 |
| 0.1767 | −0.125 | 0.5613 | −0.363 |
| 0.2524 | −0.184 | 0.6363 | −0.371 |
| 0.2933 | −0.215 | 0.6991 | −0.361 |
| 0.3442 | −0.252 | 0.7552 | −0.336 |
| 0.3801 | −0.277 | 0.8345 | −0.271 |
| 0.4443 | −0.315 | 0.9265 | −0.146 |
| o-Toluidine ($i$) + n-heptane ($j$)[c] | | | |
| 0.0814 | −0.048 | 0.5218 | −0.247 |
| 0.1663 | −0.102 | 0.5804 | −0.245 |
| 0.2224 | −0.137 | 0.6446 | −0.233 |
| 0.2812 | −0.171 | 0.7112 | −0.210 |
| 0.3388 | −0.199 | 0.7819 | −0.173 |
| 0.3991 | −0.223 | 0.8503 | −0.127 |
| 0.4554 | −0.238 | 0.9383 | −0.067 |

Also included are the various $V^{(n)}$ ($n$ = 0–2) parameters along with standard deviations, $\sigma(V^E)$.

[a] $V^{(0)} = 2.173$, $V^{(1)} = -1.202$, $V^{(2)} = 0.300$, $\sigma(V^{(E)}) = 0.005$ cm$^3$ mol$^{-1}$.
[b] $V^{(0)} = -1.370$, $V^{(1)} = -0.837$, $V^{(2)} = 0.078$, $\sigma(V^{(E)}) = 0.003$ cm$^3$ mol$^{-1}$.
[c] $V^{(0)} = -1.370$, $V^{(1)} = -0.837$, $V^{(2)} = 0.078$, $\sigma(V^{(E)}) = 0.003$ cm$^3$ mol$^{-1}$.

**Table 3**
Measured molar excess enthalpies, $H^E$ values for the various ($i+j$) mixtures as a function of mole fraction, $x_i$, of component ($i$) at 308.15 K

| $x_i$ | $H^E$ (J mol$^{-1}$) | $x_i$ | $H^E$ (J mol$^{-1}$) |
|---|---|---|---|
| o-Toluidine ($i$) + cyclohexane ($j$)[a] | | | |
| 0.0527 | 265.8 | 0.4907 | 1668.7 |
| 0.1017 | 506.4 | 0.5613 | 1666.6 |
| 0.1628 | 789.5 | 0.6121 | 1617.3 |
| 0.2349 | 1087.7 | 0.6774 | 1494.9 |
| 0.2681 | 1307.7 | 0.7643 | 1230.9 |
| 0.3614 | 1481.5 | 0.8391 | 915.8 |
| 0.4213 | 1597.8 | 0.9310 | 428.3 |
| o-Toluidine ($i$) + n-hexane ($j$)[b] | | | |
| 0.0678 | 160.9 | 0.5317 | 1463.1 |
| 0.1317 | 351.3 | 0.5997 | 1504.8 |
| 0.1927 | 553.0 | 0.6532 | 1486.0 |
| 0.2505 | 749.8 | 0.7013 | 1426.3 |
| 0.3314 | 1014.4 | 0.7717 | 1259.9 |
| 0.4015 | 1215.1 | 0.8439 | 984.7 |
| 0.4718 | 1373.2 | 0.9164 | 595.4 |
| o-Toluidine ($i$) + n-heptane ($j$)[c] | | | |
| 0.0734 | 200.4 | 0.5019 | 979.2 |
| 0.1457 | 364.8 | 0.5876 | 1070.8 |
| 0.1968 | 468.3 | 0.6513 | 1103.4 |
| 0.2678 | 601.7 | 0.7016 | 1098.3 |
| 0.3109 | 678.5 | 0.7767 | 1021.6 |
| 0.3874 | 808.3 | 0.8312 | 899.0 |
| 0.4467 | 901.5 | 0.9267 | 503.6 |

Also included are the various $H^{(n)}$ ($n$ = 0–2) parameters along with standard deviations, $\sigma(H^E)$.

[a] $H^{(0)} = 5684.9$, $H^{(1)} = 3058.4$, $H^{(2)} = -663.2$, $\sigma(H^{(E)}) = 16.2$ J mol$^{-1}$.
[b] $H^{(0)} = 6691.2$, $H^{(1)} = 735.9$, $H^{(2)} = -885.2$, $\sigma(H^{(E)}) = 15.1$ J mol$^{-1}$.
[c] $H^{(0)} = 3906.1$, $H^{(1)} = 2616.7$, $H^{(2)} = 1748.5$, $\sigma(H^{(E)}) = 11.1$ J mol$^{-1}$.

The densities, $\rho_{ij}$ of binary mixtures were determined by employing their molar excess volumes data via the following equation:

$$V^E = \left[ \frac{x_i M_i}{\rho_{ij}} + \frac{x_j M_j}{\rho_{ij}} \right] - \left[ \frac{x_i M_i}{\rho_i} + \frac{x_j M_j}{\rho_j} \right] \tag{2}$$

where $x_i$, $M_i$ and $\rho_i$ are the mole fraction, molar mass and density, respectively, of component ($i$). Isentropic compressibility changes
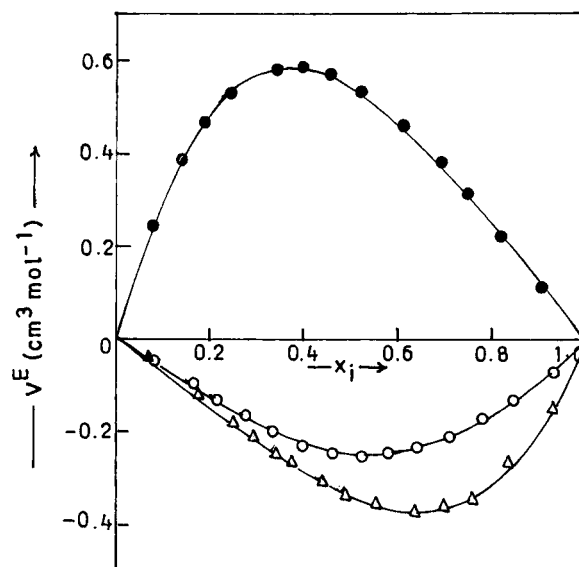


**Fig. 1.** Molar excess volumes, $V^E$ for o-toluidine ($i$) + cyclohexane ($j$), (●) o-toluidine ($i$) + n-hexane ($j$), (△) o-toluidine ($i$) + n-heptane ($j$), (○) at 308.15 K.

**Table 4**
Speeds of sound, $u$, isentropic compressibilities, $\kappa_S$, and isentropic compressibility changes of mixing, $\kappa_S^E$ for the various $(i+j)$ mixtures as a function of composition, $x_i$, mole fraction of component $(i)$ at 308.15 K

| $x_i$ | $u$ (m s$^{-1}$) | $\kappa_S$ (TPa$^{-1}$) | $\kappa_S^E$ (TPa$^{-1}$) |
|---|---|---|---|
| *o*-Toluidine $(i)$ + cyclohexane $(j)$[a] | | | |
| 0.0663 | 1215 | 874.3 | 10.5 |
| 0.1293 | 1221 | 853.9 | 15.4 |
| 0.1758 | 1228 | 835.7 | 16.5 |
| 0.2355 | 1239 | 809.5 | 15.5 |
| 0.2902 | 1252 | 783.0 | 12.8 |
| 0.3335 | 1264 | 760.8 | 9.9 |
| 0.3930 | 1282 | 728.9 | 5.2 |
| 0.4881 | 1315 | 676.1 | −2.5 |
| 0.5560 | 1342 | 637.6 | −7.4 |
| 0.6453 | 1382 | 587.5 | −11.9 |
| 0.7117 | 1415 | 550.4 | −13.4 |
| 0.7986 | 1462 | 503.0 | −12.8 |
| 0.8479 | 1493 | 476.1 | −11.0 |
| 0.9026 | 1528 | 446.9 | −8.0 |
| *o*-Toluidine $(i)$ + *n*-hexane $(j)$[b] | | | |
| 0.0697 | 1056 | 1355.6 | −53.8 |
| 0.1172 | 1075 | 1284.6 | −88.6 |
| 0.1851 | 1105 | 1186.1 | −133.9 |
| 0.2657 | 1142 | 1075.9 | −178.1 |
| 0.3119 | 1165 | 1015.7 | −197.9 |
| 0.3707 | 1194 | 944.9 | −216.5 |
| 0.4478 | 1232 | 859.0 | −228.9 |
| 0.5009 | 1259 | 805.3 | −229.4 |
| 0.5787 | 1297 | 734.3 | −218.5 |
| 0.6449 | 1329 | 679.2 | −199.1 |
| 0.7090 | 1359 | 630.4 | −172.3 |
| 0.7673 | 1389 | 588.1 | −142.2 |
| 0.8391 | 1433 | 534.3 | −100.2 |
| 0.9123 | 1501 | 469.7 | −60.5 |
| *o*-Toluidine $(i)$ + *n*-heptane $(j)$[c] | | | |
| 0.0707 | 1102 | 1197.2 | −17.3 |
| 0.1227 | 1115 | 1148.2 | −31.2 |
| 0.1758 | 1129 | 1098.2 | −45.4 |
| 0.2378 | 1148 | 1038.6 | −60.9 |
| 0.3079 | 1172 | 971.8 | −75.9 |
| 0.3008 | 1187 | 932.4 | −83.3 |
| 0.4047 | 1208 | 883.1 | −90.2 |
| 0.4679 | 1233 | 827.7 | −94.6 |
| 0.5470 | 1266 | 760.7 | −94.2 |
| 0.6131 | 1296 | 707.3 | −88.8 |
| 0.6884 | 1334 | 648.6 | −77.5 |
| 0.7597 | 1373 | 594.4 | −62.5 |
| 0.8208 | 1413 | 547.4 | −47.3 |
| 0.9224 | 1501 | 465.1 | −19.8 |

Also included are the various $\kappa_S^{(n)}$ ($n=0$–2) parameters along with standard deviations, $\sigma(\kappa_S^E)$.

[a] $\kappa_S^{(0)} = 44.1$, $\kappa_S^{(1)} = -364.3$, $\kappa_S^{(2)} = 46.1$, $\sigma(\kappa_S^E) = 0.1$.

[b] $\kappa_S^{(0)} = -917.9$, $\kappa_S^{(1)} = 99.7$, $\kappa_S^{(2)} = 235.3$, $\sigma(\kappa_S^E) = 2.3$.

[c] $\kappa_S^{(0)} = -380.9$, $\kappa_S^{(1)} = -5.4$, $\kappa_S^{(2)} = 153.0$, $\sigma(\kappa_S^E) = 0.9$.

of mixing, $\kappa_S^E$ were determined from relation:

$$\kappa_S^E = \kappa_S - \sum_{i=i}^{j} \phi_i(\kappa_S)_i \tag{3}$$

where $\phi_i$ and $(\kappa_S)_i$ are the volume fraction and isentropic compressibility of component $(i)$. The resulting $\kappa_S^E$ values for the studied mixtures are recorded in Table 4 and are plotted in Fig. 3.

For each binary mixture, $V^E$, $H^E$ and $\kappa_S^E$ values were fitted to the following equation:

$$X^E(X = V \text{ or } H \text{ or } \kappa_S) = x_i x_j [X^{(0)} + X^{(1)}(2x_i - 1) + X^{(2)}(2x_i - 1)^2] \tag{4}$$

where $X^{(n)}$ ($n=0$–2) are parameters characteristic of a binary $(i+j)$ mixture that were evaluated by the least squares method and are recorded along with their standard deviations, $\sigma(X^E: X=V \text{ or } H \text{ or }$
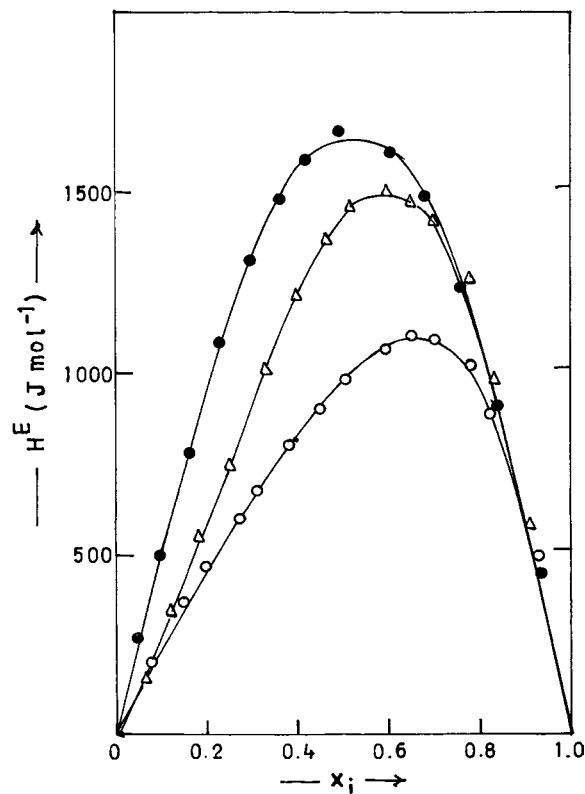


**Fig. 2.** Molar excess enthalpies, $H$ for *o*-toluidine $(i)$ + cyclohexane $(j)$, (#) *o*-toluidine $(i)$ + *n*-hexane $(j)$, ($\triangle$) *o*-toluidine $(i)$ + *n*-heptane $(j)$, ($\bigcirc$) at 308.15 K.
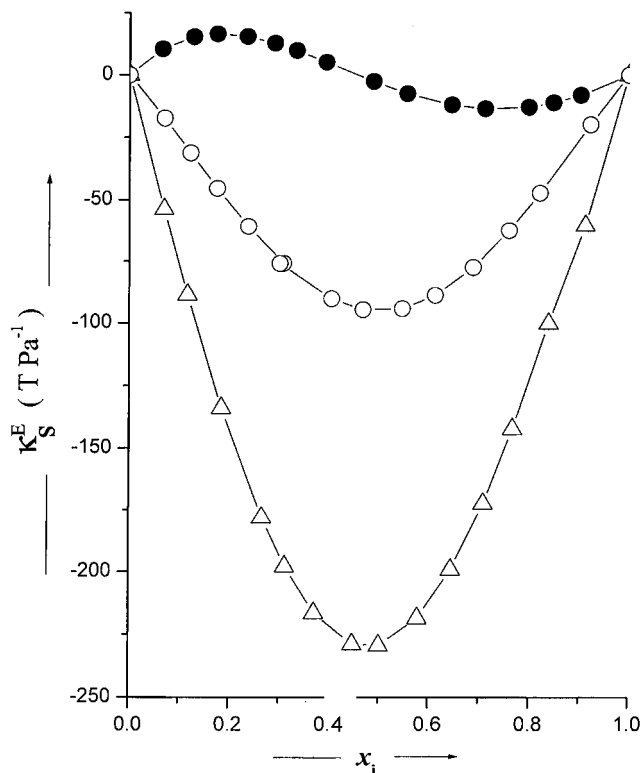


**Fig. 3.** Isentropic compressibility change of mixing, $\kappa_S^E$ for *o*-toluidine $(i)$ + cyclohexane $(j)$, ($\bullet$) *o*-toluidine $(i)$ + *n*-hexane $(j)$, ($\triangle$) *o*-toluidine $(i)$ + *n*-heptane $(j)$, ($\bigcirc$) at 308.15 K.

$\kappa_S$) of $X^E$ defined by

$$\sigma(X^E : X = V \text{ or } H \text{ or } \kappa_S) = [(X^E)_{\text{exptl}} - (X^E)_{\text{calc.Eq.(4)}}] \qquad (5)$$

[$(X^E)_{\text{calc. Eq. (4)}}$ are the values evaluated by employing Eq. (4), $m$ is the number of data points, and $n$ is the number of adjustable parameters] in Tables 2–4.

## 4. Discussion

We are unaware of any $V^E$, $H^E$ and $\kappa_S^E$ data of OT ($i$) + cyclohexane or $n$-hexane or $n$-heptane ($j$) binary mixtures at 308.15 K with which to compare our results, $H^E$ data of binary OT ($i$) + cyclohexane or $n$-hexane or $n$-heptane ($j$) mixtures are positive over the entire range of composition. $V^E$ and $\kappa_S^E$ data of OT ($i$) + $n$-hexane or $n$-heptane ($j$) mixture are negative over whole composition range. While sign of $V^E$ values of OT ($i$) + cyclohexane ($j$) mixture is positive over whole mole fraction range; sign of $\kappa_S^E$ values changes from positive to negative with increase in mole fraction of OT ($i$).

$H^E$ data of OT ($i$) + $n$-hexane or $n$-heptane ($j$) mixtures may be rationalized if it be assumed that (1) OT ($i$) is an associated molecular entity in pure state and there is establishment of unlike contacts between $i$ and $j$, (2) unlike contacts then influences $i$–$i$ interaction that leads to the depolymerization of $i_n$ to yield respective $i$-monomers, and (3) the monomers of $i$ and $j$ then undergoes dipole-induced dipole interactions to form $i$:$j$. molecular entity. $H^E$ data for ($i$ + $j$) mixtures suggest that contribution due to factor (2) far overweigh the contribution due to factors (1) and (3). $H^E$ values of OT ($i$) + $n$-hexane ($j$) mixtures are higher than those OT ($i$) + $n$-heptane ($j$) mixtures. This may be due to an increase in C—C

chain length of $n$-hexane which in turn leads to increase in dipole-induced dipole interactions. $H^E$ values of OT ($i$) + cyclohexane ($j$) mixture reveals that addition of cyclohexane to OT results in the depolymerization of OT.

$V^E$ and $\kappa_S^E$ data of ($i$ + $j$) mixtures suggest that addition of $n$-alkanes to OT ($i$) gives relatively more packed structure than cyclohexane in OT.

### 4.1. Conceptual aspects of Graph theory and results

According to mathematical discipline of Graph theory, if atoms in the structural formula of a molecule are represented by vertices and the bonds joining them by lines, then the resulting graph of a molecule describes the topology of the molecule [2–4,16,17]. Consequently if $\delta_m^v$, $\delta_n^v$, $\delta_o^v$, $\delta_p^v$, etc. denotes the valency for forming bonds of the $m$th, etc. vertex in the molecular graph, then connectivity parameter, $^3\xi$, of third degree is defined by the following equation:

$$^3\xi = \sum_{m<n<o<p} (\delta_m^v \delta_n^v \delta_o^v \delta_p^v)^{-0.5} \qquad (6)$$

Singh et al [18] have postulated that $(^3\xi)^{-1}$ value of a molecule represents a measure of probability that the surface of one molecule interacts effectively with the surface of another molecules, and $^3\xi$ values can be employed to predict $V^E$, $H^E$ and $\kappa_S^E$ of binary and ternary mixtures [5,10]. The $^3\xi$ values of the constituents of the mixtures depends on the valencies of various vertices in their molecular graph, the addition of $j$ to $i$ would cause structural changes in their topology. As, $V^E$, is a packing effect. So $V^E$ of ($i$ + $j$) mixture would reflect change in topology of $i$ or $j$. Thus, it is of interest to analyze

**Table 5**
Comparison of $V^E$, $H^E$ and $\kappa_S^E$ values calculated from appropriate equations with their corresponding experimental values at 308.15 K

| | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 |
|---|---|---|---|---|---|---|---|---|---|
| *o*-Toluidine ($i$) + cyclohexane ($j$)[a] | | | | | | | | | |
| $V^E$ (Exptl) | 0.299 | 0.480 | 0.567 | 0.582 | – | 0.467 | 0.365 | 0.250 | 0.126 |
| $V^E$ (Graph) | 0.220 | 0.380 | 0.481 | 0.540 | – | 0.506 | 0.433 | 0.321 | 0.174 |
| $V^E$ (Flory) | 0.453 | 0.857 | 1.204 | 1.485 | – | 1.789 | 1.762 | 1.563 | 1.118 |
| $H^E$ (Exptl) | 498.3 | 949.0 | 1313.6 | 1562.1 | – | 1632.7 | 1437.2 | 1090.2 | 604.2 |
| $H^E$ (Graph) | 538.9 | 1261.2 | 1351.0 | – | – | 1654.1 | 1492.3 | 1173.4 | 639.4 |
| $H^E$ (Flory) | 49.7 | 95.6 | 141.9 | 192.4 | – | 319.4 | 401.1 | 497.2 | 608.1 |
| $\kappa_S^E$ (Exptl) | 13.7 | 16.4 | 12.2 | – | – | −9.9 | −13.3 | −12.8 | −8.1 |
| $\kappa_S^E$ (Graph) | 9.8 | 12.9 | 10.7 | – | – | −11.7 | −12.0 | −20.1 | −15.1 |
| $\kappa_S^E$ (Flory) | −31.7 | −59.6 | −77.1 | −85.5 | – | −79.4 | −66.7 | −48.5 | −25.4 |
| *o*-Toluidine ($i$) + $n$-hexane ($j$)[b] | | | | | | | | | |
| $V^E$ (Exptl) | −0.067 | −0.143 | −0.220 | −0.289 | – | −0.370 | −0.361 | −0.304 | −0.188 |
| $V^E$ (Graph) | −0.105 | −0.232 | −0.297 | −0.334 | – | −0.318 | −0.270 | −0.205 | −0.111 |
| $V^E$ (Flory) | 1.018 | −1.660 | −2.002 | −2.102 | – | −1.753 | −1.374 | −0.892 | −0.330 |
| $H^E$ (Exptl) | 253.2 | 577.8 | 914.6 | 1211.2 | – | 1504.8 | 1428.5 | 1165.0 | 693.6 |
| $H^E$ (Graph) | 296.0 | 615.9 | 931.4 | – | – | 1457.9 | 1481.2 | 1246.0 | 770.2 |
| $H^E$ (Flory) | 34.3 | 77.3 | 130.3 | 193.4 | – | 346.7 | 433.7 | 524.7 | 616.6 |
| $\kappa_S^E$ (Exptl) | −76.2 | −142.9 | −193.2 | – | – | −213.2 | −176.5 | −123.7 | −61.9 |
| $\kappa_S^E$ (Graph) | −86.4 | −152.2 | −197.6 | – | – | −218.6 | −188.9 | −142.0 | −78.9 |
| $\kappa_S^E$ (Flory) | −77.3 | −135.9 | −172.0 | −188.6 | – | −173.5 | −145.7 | −106.3 | −56.8 |
| *o*-Toluidine ($i$) + $n$-heptane ($j$)[c] | | | | | | | | | |
| $V^E$ (Exptl) | −0.059 | −0.123 | −0.180 | −0.223 | – | −0.243 | −0.215 | −0.162 | −0.088 |
| $V^E$ (Graph) | −0.097 | −0.171 | −0.219 | −0.242 | – | −0.242 | −0.197 | −0.146 | −0.083 |
| $V^E$ (Flory) | 0.454 | 0.771 | 0.973 | 0.076 | – | 1.035 | 0.910 | 0.726 | 0.487 |
| $H^E$ (Exptl) | 263.9 | 474.6 | 659.4 | 828.8 | – | 1080.9 | 1098.9 | 976.9 | 640.7 |
| $H^E$ (Graph) | 198.8 | 417.0 | 634.1 | – | – | 1002.2 | 1025.0 | 865.0 | 536.4 |
| $H^E$ (Flory) | 41.3 | 83.7 | 127.5 | 173.0 | – | 269.5 | 320.4 | 372.8 | 426.3 |
| $\kappa_S^E$ (Exptl) | −25.1 | −54.8 | −74.4 | – | – | −90.2 | −75.3 | −55.8 | −25.9 |
| $\kappa_S^E$ (Graph) | −31.9 | −57.7 | −77.1 | – | – | −93.2 | −83.2 | −64.7 | −37.1 |
| $\kappa_S^E$ (Flory) | −164.4 | −251.8 | −289.9 | −295.1 | – | −242.0 | −194.2 | −136.5 | −70.9 |

Also included are various $(^3\xi_i)$ and $(^3\xi_i)_m$ ($i = i$ or $j$) ; $\alpha_{ij}$ and the interaction energy parameters $\chi_{ij}$, $\chi_{ii}$ and $\chi_{ij}^*$.

[a] $(^3\xi_i) = (^3\xi_i)_m = 2.001$; $(^3\xi_i) = (^3\xi_i)_m = 1.500$; $\alpha_{ij} = -45.740$; $\chi_{ij} = 5833.6 \text{ J mol}^{-1}$; $\chi_{ii} = 38.8 \text{ J mol}^{-1}$; $\chi_{ij}^* = 16.2 \text{ J mol}^{-1}$; $\chi_{ij} = 135.7 \text{ T Pa}^{-1}$; $\chi_{ii} = -295.2 \text{ T Pa}^{-1}$.

[b] $(^3\xi_i) = (^3\xi_i)_m = 1.201$; $(^3\xi_i) = (^3\xi_i)_m = 0.957$; $\alpha_{ij} = 28.501$; $\chi_{ij} = 2749.8 \text{ J mol}^{-1}$; $\chi_{ii} = 4719.9 \text{ J mol}^{-1}$; $\chi_{ij}^* = 14.8 \text{ J mol}^{-1}$; $\chi_{ij} = -968.3 \text{ T Pa}^{-1}$; $\chi_{ii} = 280.6 \text{ T Pa}^{-1}$.

[c] $(^3\xi_i) = (^3\xi_i)_m = 1.401$; $(^3\xi_i) = (^3\xi_i)_m = 1.100$; $\alpha_{ij} = 16.333$; $\chi_{ij} = 1832.7 \text{ J mol}^{-1}$; $\chi_{ii} = 3308.9 \text{ J mol}^{-1}$; $\chi_{ij}^* = 9.4 \text{ J mol}^{-1}$; $\chi_{ij} = -348.6 \text{ T Pa}^{-1}$; $\chi_{ii} = 17.2 \text{ T Pa}^{-1}$.
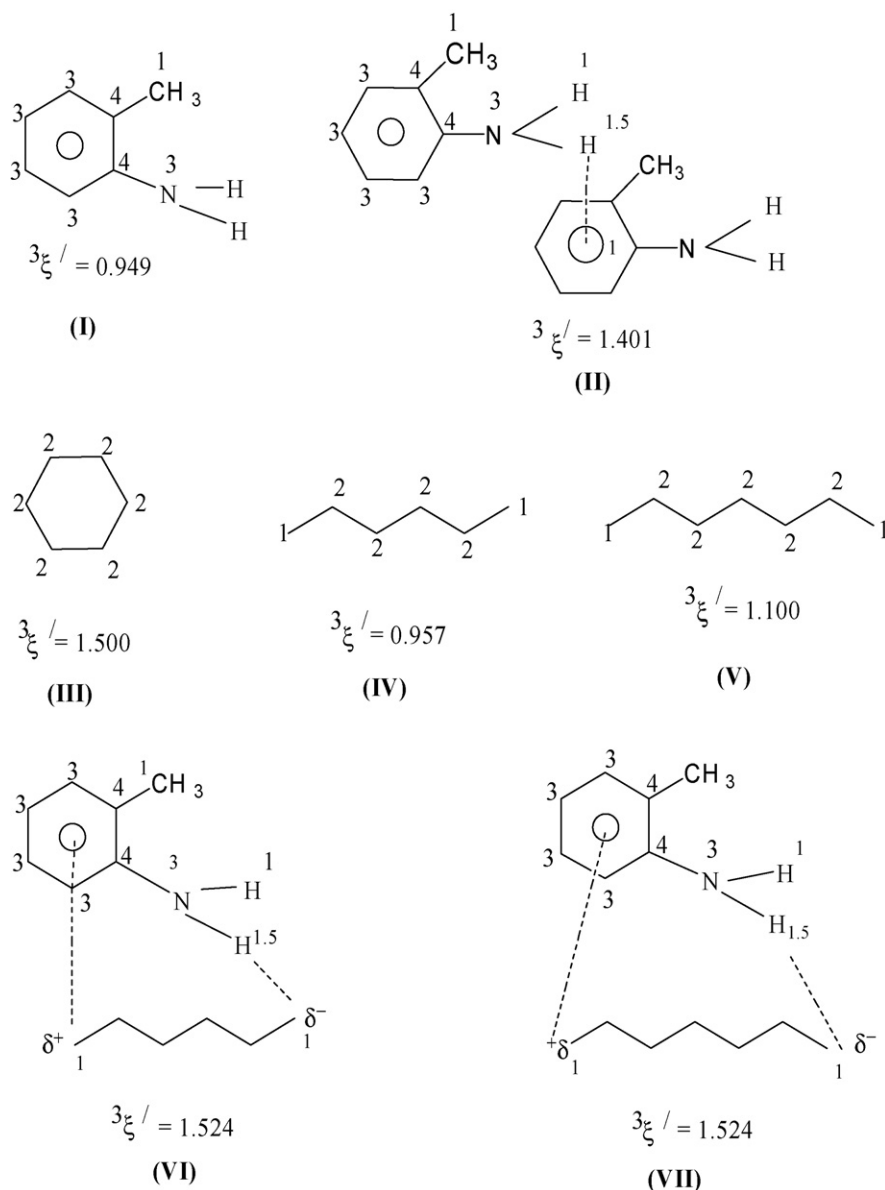
**Scheme 1.** : Connectivity parameters of various molecular entities.

$V^E$ data of $(i+j)$ mixtures in terms of Graph theory. According to this theory, $V^E$ is given by

$$V^E = \alpha_{ij} \left[ \sum x_i (^3\xi_i)_m^{-1} - \sum x_i (^3\xi_i)^{-1} \right] \tag{7}$$

$\alpha_{ij}$ is a constant characteristic of $(i+j)$ mixture, $^3\xi_i$ and $(^3\xi_i)_m$ $(i = i$ or $j)$, etc. are connectivity parameters of third degree in pure and mixed state.

As degree of association of $i/j$ is not known, $^3\xi_i$ and $(^3\xi_i)_m$ $(i = i$ or $j)$, etc. parameters were regarded as adjustable parameters and were predicted by fitting experimental $V^E$ data to Eq. (7). Only those $^3\xi_i$ and $(^3\xi_i)_m$ $(i = i$ or $j)$ values were retained that best reproduced the experimental $V^E$ data. Such $^3\xi_i$, $(^3\xi_i)_m$ $(i = i$ or $j)$, etc. values along with $V^E$ values (calculated via Eq. (7)) at various $x_i$ are recorded in Table 5 and $V^E$ values are also compared with their corresponding experimental values. Examination of data in Table 5 reveals that calculated $V^E$ values compare well with their corresponding values. Since the agreement between experimental and calculated values is good ($^3\xi_i$), etc. values can be relied upon to extract information about the state of components $i/j$ in pure and mixed state.

A number of structures were assumed for OT in pure state and there $^3\xi^l$ values were determined from structural consideration (via Eq. (6)). These $^3\xi^l$ values were then compared with $^3\xi$ values (evaluated from Eq. (7)). Any structure or combination of structures that yielded $^3\xi^l$ values (calculated from Eq. (6)) that compare well with $^3\xi$ values in Table 5 was taken to be a representative structure of that component. Such an analysis revealed that OT in pure state exist as an associated molecular entity **II** ($^3\xi^l = 1.401$). $^3\xi_j$ values of 1.500, 0.957 and 1.100 for cyclohexane, $n$-hexane and $n$-heptane suggest that they exists as a monomer [molecular entities **III**–**V**]. $(^3\xi^l_i)_m$ values were next evaluated to extract information about the state of OT ($i$) in $n$-hexane or $n$-heptane. It was assumed that studied $(i+j)$ mixtures may contain molecular entities **VI** and **VII**. For this purpose, it was assumed that these molecular entities **VI** and **VII** are characterized by dipole-induced-dipole interaction. $(^3\xi^l_i)_m$ for molecular entities **VI** and **VII** were then calculated be 1.524. $(^3\xi_i)_m$

values of 1.201 and 1.401 (Table 4) for OT ($i$) + $n$-hexane or $n$-heptane ($j$) mixtures suggest the presence of molecular entities **VI** and **VII** in the studied mixtures (Scheme 1).

$H^E$ and $\kappa_S^E$ of ($i+j$) mixtures have next been analyzed in terms of Graph theory. If $\chi_{ij}$, $\chi_{ii}$, and $\chi_{12}$ are molar energy and molar compressibility parameters for $i$–$j$, $i$–$i$ and dipole-induced dipole interactions, respectively, then change in molar thermodynamic property, $\Delta X$ ($X = H$ or $\kappa_S$) due to processes (1)–(3) discussed in qualitative analysis of $H^E$ data of these mixtures is given [19–21] by relations:

$$\Delta X_1(X = H \text{ or } \kappa_S) = x_i \chi_{ij} S_j \tag{8}$$

where $S_j$ is the surface fraction of ($j$), defined [19] by

$$S_j = \frac{x_j v_j}{\sum_{i=i}^{j} x_i v_i} \tag{9}$$

so that

$$\Delta X_1(X = H \text{ or } \kappa_S) = \frac{x_i x_j v_j \chi_{ij}}{\sum x_i v_i} \tag{10}$$

$$\Delta X_2(X = H \text{ or } \kappa_S) = \frac{x_i^2 x_j v_j \chi_{ii}}{\sum_{i=i}^{j} x_i v_i} \tag{11}$$

$$\Delta X_3(X = H \text{ or } \kappa_S) = \frac{x_i x_j^2 v_j \chi_{12}}{\sum x_i v_i} \tag{12}$$

where $v_j$ is the molar volume of component ($j$). The overall excess thermodynamic property, $X^E$ ($X = H$ or $\kappa_S$) for various ($i+j$) mixtures is expressed by relation:

$$X^E(X = H \text{ or } \kappa_S) = \sum_{i=1}^{3} \Delta X_i = \left[ \frac{x_i x_j v_j}{\sum x_i v_i} \right] [\chi_{ij} + x_i \chi_{ii} + x_j \chi_{12}] \tag{13}$$

Further, $v_j/v_i = {}^3\xi_i/{}^3\xi_j$ [18], Eq. (13) then reduces to

$$X^E(X = H \text{ or } \kappa_S) = \left[ \frac{x_i x_j({}^3\xi_i/{}^3\xi_j)}{x_i + x_j({}^3\xi_i/{}^3\xi_j)} \right] [\chi_{ij} + x_i \chi_{ii} + x_j \chi_{12}] \tag{14}$$

For the studied mixtures, if it be assumed that $\chi_{ij} \gg \chi_{12} = \chi_{ij}$, then Eq. (14) can be expressed by

$$X^E(X = H \text{ or } \kappa_S) = \left[ \frac{x_i x_j({}^3\xi_i/{}^3\xi_j)}{x_i + x_j({}^3\xi_i/{}^3\xi_j)} \right] [\chi_{ij} + x_i \chi_{ii}] \tag{15}$$

Eq. (15) contains two unknown parameters ($\chi_{ij}$ and $\chi_{ii}$) and for the present analysis, we employed $X^E$ ($X = H$ or $\kappa_S$) data at two compositions ($x_i = 0.4$ and 0.5) to predict these parameters. These parameters were then utilized to predict $X^E$ ($X = H$ or $\kappa_S$) data at various of values of $x_i$. Such $H^E$ and $\kappa_S^E$ values along with $\chi_{ij}$, etc. parameters are recorded in Table 5 and are also compared with their corresponding experimental values.

Examination of data in Table 5 reveals that $H^E$ and $\kappa_S^E$ values compare reasonably well with their corresponding experimental values. This lends additional support to the basic assumptions made in deriving Eq. (15).

$V^E$, $H^E$ and $\kappa_S^E$ data for the investigated binary mixtures have also been analyzed in terms of Flory theory. According to Flory's theory [22,23] $V^E$ and $H^E$ for binary mixture is given by the following equations:

$$V^E = \bar{V}_{\text{cal}}^E \left[ \sum_{i=i}^{j} x_i v_i^* \right] \tag{16}$$

$$H^E = \sum x_i P_i^* \left( \bar{V}_i^{-1} - \bar{V}_{\text{cal}}^{-1} \right) + x_i V_i^* \theta_j \chi_{ij}^* \bar{V}_{\text{cal}}^{-1} \tag{17}$$

where

$$\bar{v}_i = \left[ \frac{1 + \alpha_i(T/3)}{(1 + \alpha_i T)^3} \right]^3 \tag{18}$$

$$\bar{V}_{\text{cal}}^E = \bar{v}_0^{7/3} [\tfrac{4}{3} - (\bar{v}_0)^{1/3}]^{-1} [\bar{T} - \bar{T}_0] \tag{19}$$

$$\bar{T}_0 = \frac{\bar{v}_0^{1/3} - 1}{\bar{v}_0^{4/3}} \tag{20}$$

$$\bar{v}_i^* = \frac{v_i}{\bar{v}_i} \tag{21}$$

$$\bar{v}_0 = \sum \phi_i v_i^* \tag{22}$$

$$T = \left[ \frac{\sum \phi_i P_i^* \bar{T}_i}{\sum \phi_i P_i^*} \right] \left[ 1 - (\phi_i \theta_j \chi_{ij}^*) \left( \sum \phi_i P_i^* \right)^{-1} \right]^{-1} \tag{23}$$

$$\bar{T}_i = \frac{\bar{v}_i^{1/3} - 1}{\bar{v}_i^{4/3}} \tag{24}$$

$$P^* = \sum \phi_i P_i^* - \sum \phi_i^* \theta_j \chi_{ij}^* \tag{25}$$

$$P_i^* = \alpha_i T \bar{v}_i^2 [(\kappa_T)_i]^{-1} \tag{26}$$

all the terms have same significance as described elsewhere [22,23].

Evaluation of $V^E$ and $H^E$ by Flory theory requires a knowledge of reduced temperature, $\bar{T}$, which in turn depends upon adjustable parameters $\theta_j \chi_{ij}^*$, etc. of binary mixtures. These parameters were determined by fitting $H^E$ values at $x_i = 0.5$ to Eq. (17). Various parameters of pure components were determined using isothermal compressibility, $\kappa_T$ reported in literature [24]. $\kappa_T$ values for OT were calculated by employing $\Delta H_V$ values in the manner as suggested by Hilderbrand et al. [25]. Such $V^E$ and $H^E$ values evaluated via Eqs. (16)–(26) along with $\chi_{ij}^*$, etc. parameters are recorded in Table 5 and are also compared with their corresponding experimental values.

According to Flory's theory, $\kappa_S^E$ is expressed by the relation:

$$\kappa_S^E = \kappa_S - \kappa_S^{\text{id}} \tag{27}$$

The isentropic compressibility, $\kappa_S$, of ($i+j$) binary mixture, at effectively zero pressure is expressed by the following equation:

$$\kappa_S = \kappa_T - T \frac{v_m^* \alpha_p^2}{C_{p,m}} \tag{28}$$

The isothermal compressibility, $\kappa_T$, of a mixture at effectively zero pressure is given by the following equation:

$$\kappa_T = \left[ \left( \frac{3\bar{v}_m^2}{p^*} \right) \frac{\bar{v}_m^{1/3} - 1}{4 - 3\bar{v}_m^{1/3}} \right] \tag{29}$$

where

$$v_m^* = \sum_{i=i}^{j} \phi_i v_i^* \tag{30}$$

$$\alpha_p = 3 \frac{\bar{v}_m^{1/3} - 1}{T(4 - 3\bar{v}_m^{1/3})} \tag{31}$$

$$p^* = \sum_{i=i}^{j} \phi_i p_i^* - \sum_{i=i}^{k} \phi_i \theta_j \chi_{ij}^* \tag{32}$$

$$\bar{v} = \frac{v}{v^*} \tag{33}$$

$$\bar{v}_m = \sum_{i=i}^{j} \phi_i v_i^* \tag{34}$$

$$C_{p,m} = \left( \frac{\partial H^E}{\partial T} \right) + \sum_{i=i}^{k} x_i C_{p,i} \tag{35}$$

where $\bar{v}$, $v^*$ and $c_{p,i}$ represent the reduced volume, characteristic volume, and molar heat capacities of component ($i$) in binary mixtures. ($\partial H^E/\partial T$) values were determined by predicting $H^E$ values at 298.15 K for OT ($i$) + cyclohexane or $n$-hexane or $n$-heptane ($j$) binary mixtures in the manner described elsewhere [26]. $\kappa_S^{id}$ values for the corresponding ideal mixtures were calculated using Eq. (28). While $\alpha_p^{id}$ and $c_{p,m}^{id}$ were taken as mole fraction average; $\kappa_S^{id}$ were taken as volume fraction average. Such $\kappa_S^E$ values calculated for the present binary mixtures are recorded in Table 5 and are also compared with their corresponding experimental values.

A perusal of data in Table 5 reveals that Flory theory correctly predicts the sign of $H^E$ and $\kappa_S^E$ values for OT ($i$) + $n$-hexane or $n$-heptane ($j$) binary mixtures. However theory fails to predicted sign of $\kappa_S^E$ values for OT ($i$) + cyclohexane ($j$) and $V^E$ value for OT ($i$) + $n$-heptane ($j$) mixtures. The failure of theory to correctly predict the magnitude of $V^E$, $H^E$ and $\kappa_S^E$ may be due to various assumptions made in evaluating various parameters which were not reported in the literature but have been determined theoretically and also due to the nature of components in these mixtures.

## Acknowledgements

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