Thermodynamic interactions in binary mixtures of 1-chloronaphthalene and monocyclic aromatics

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Thermodynamic interactions in binary mixtures of 1-chloronaphthalene with the monocyclic aromatics have been studied through calculation of excess molar volumes from Flory equation of state and that of Prigogine-Flory-Patterson theories using the experimental results of density, viscosity and speed of sound. The experimental excess viscosity has been compared with Bloomfield-Dewan theory, while the excess isentropic and isothermal compressibilities have been analysed using Benson-Kiyohara theory. Efforts have also been made to calculate the excess internal pressure from Prigogine-Saraga theory. All the excess quantities have been fitted to Redlich-Kister equation to estimate the binary coefficients and standard deviations.

Thermodynamic interactions in binary liquid mixtures containing 1-chloronaphthalene (1-CN) has received considerable attention. However, binary mixtures of 1-chloronaphthalene with monocyclic aromatics such as benzene, methyl-benzene, 1,4-dimethylbenzene, 1,3,5-trimethylbenzene and methoxybenzene have not been studied earlier. Such mixtures are important from the viewpoint of understanding the intermolecular interactions. Herein, we present calculated values of excess molar volume, \( V^E \), excess viscosity, \( \eta^E \), excess Gibbs energy of activation of flow, \( G^E \), excess isentropic compressibility, \( k_i^E \) and excess isothermal compressibility, \( k_i^E \) obtained using reported data of density, \( \rho \), viscosity, \( \eta \), speed of sound, \( u \) and refractive index, \( n_0 \) at 298.15 K, published earlier.

Theoretical

Flory theory

Excess molar volume, \( V^E \), has been calculated from the Flory equation of state as:

\[
V^E = \left( \sum_{i=1}^{2} \chi_i V_i^0 \right) \left( \frac{\tilde{V}^0_1^{7/3}}{[4/3 - (\tilde{T}^0_1)^{1/3}]} \right) (\tilde{T} - \tilde{T}^0) \quad \ldots (1)
\]

where \( \tilde{V}^0_1 \) is given by

\[
\tilde{V}^0_1 = \frac{V^0_1}{V_1} \quad \ldots (2)
\]

Here, \( V_i^0 \) is the characteristic volume of the i-th component in the mixture. Reduced volume, \( \tilde{V} \) is calculated from thermal expansion coefficient, \( \alpha = -(1/\rho)(\partial \rho / \partial T)_p \) using relation:

\[
\tilde{V} = \left[ 1 + \frac{4}{3} \alpha T \right] \\
(1 + \alpha T) \quad \ldots (3)
\]

Reduced temperature, \( \tilde{T} \) and the ideal reduced temperature, \( \tilde{T}^0 \) in Eq. (1) are calculated as:

\[
\tilde{T}^0 = \left( \frac{\tilde{V}^{0-1/3} - 1}{\tilde{V}^{0+1/3}} \right) \quad \ldots (4)
\]

The \( \tilde{T} \) of the mixture is then calculated as:

\[
\tilde{T} = \left( \frac{\phi_1 P_1^* \tilde{T}_1 + \phi_2 P_2^* \tilde{T}_2}{\phi_1 P_1^* + \phi_2 P_2^*} \right) \quad \ldots (5)
\]

where the segment or hard-core volume fraction, \( \phi_i \).
is calculated as:
\[ \phi_2 = 1 - \phi_1 = 1 - \frac{x_1 V_1^*}{\sum (x_i V_i^*)} \]  \hspace{1cm} (6)

The characteristic pressure, \( P^* \), is calculated using Eq. 7.
\[ P^* = \frac{T \bar{V}^2 \alpha}{k_T} \]  \hspace{1cm} (7)

where \( k_T \) is computed from isentropic compressibility, \( k_s \), and heat capacity, \( C_p \) of liquids using the relation:
\[ k_T = k_s + \frac{T \alpha^2 V}{C_p} \]  \hspace{1cm} (8)

The values of \( \alpha \) have been calculated from the experimental densities at different temperatures (see Table 1).

**Prigogine-Flory-Patterson (PFP) theory**

The PFP theory was used to compute \( V^E \) of the mixtures.
\[ \frac{V^E}{(x_1 V_1^* + x_2 V_2^*)} = \frac{\bar{V}^{1/3}}{[(4/3) \bar{V}^{1/3} - 1]} \psi_1 \psi_2 \left( \frac{X_{12}}{P_1^* + P_2^*} \right) \frac{[\bar{V}^{1/3} - 1]}{(P_1^* \psi_1 \psi_2 + P_2^* \psi_2 \psi_1)} \]  \hspace{1cm} (9)

The first term of Eq. (9) represents the intermolecular contribution \( \Delta V_{im}^E \) to \( V^E \), i.e., \( X_{12} \) parameter, often called contact interaction parameter; the second term is the difference in "free volume", \( \Delta V_{free}^E \), while the third term is the internal pressure contribution \( \Delta V_{p^*} \), i.e., \( p^* \) effect to \( V^E \). In order to compute \( V^E \) from Eq. (9), we have used the values given in Table 1. The surface site fraction, \( \theta_2 \), was calculated as:
\[ \theta_2 = 1 - \theta_1 = \frac{\phi_2}{\phi_2 + \phi_1 \left( \frac{V^*_2}{V^*} \right)^{1/3}} \]  \hspace{1cm} (10)

and the contact energy fraction, \( \psi_1 \), was calculated as:
\[ \psi_1 = 1 - \psi_2 = \frac{x_1 P_1 V^*_1}{\sum (x_i P_i V^*_i)} \]  \hspace{1cm} (11)

Next, by following the Flory theory, excess enthalpy, \( H^E \), and excess free energy, \( G^E \), have been calculated using the following equations:
\[ H^E = \sum_{i=1}^2 x_i P_i V^*_i \left( \frac{1}{V^*_i} - \frac{1}{\bar{V}} \right) + x_1 \theta_1 V^*_1 X_{12} \]  \hspace{1cm} (12)
\[ S^E = -\frac{x_1 P_1 V^*_1}{T_1} \left( \frac{\bar{V}^{1/3} - 1}{\bar{V}^{1/3} - 1} \right) \]  \hspace{1cm} (13)
\[ G^E = \sum_{i=1}^2 x_i P_i V^*_i \left( \frac{1}{V^*_i} - \frac{1}{\bar{V}} \right) + x_1 \theta_1 V^*_1 X_{12} \]  \hspace{1cm} (14)

**Internal pressure**

Internal pressure of liquids and liquid mixtures has been the subject of active interest in the literature. Internal pressure, \( P_i \), can be estimated from the speed of sound data in conjunction with other thermodynamic parameters.
\[ P_i = \frac{2^{1/6} RT}{2^{1/6} V - \frac{dN}{V^{1/3}}} \]  \hspace{1cm} (15)

where \( V \) (m\(^3\)/10\(^6\) mol\(^{-1}\)), \( N \) (6.023 \times 10\(^{23}\) molecules/mole) and \( d \) (calculated in SI units) are
Table 2 — Comparison of experimental speed of sound (m/s) with those calculated from Benson-Kiyohara theory at 298.15 K

1-Chloronaphthalene(1) + Benzene(2)

<table>
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<tr>
<th>$x_1$</th>
<th>Expt</th>
<th>Theo</th>
<th>$x_1$</th>
<th>Expt</th>
<th>Theo</th>
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1-Chloronaphthalene(1) + 1,4-Dimethylbenzene(2)

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1-Chloronaphthalene(1) + 1,3,5-Trimethylbenzene(2)

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<th>Theo</th>
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<th>Expt</th>
<th>Theo</th>
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1-Chloronaphthalene(1) + Methoxybenzene(2)

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respectively, molar volume, Avogadro number and molecular diameter; $R$ is molar gas constant in SI units and $T$ is temperature in Kelvin. Values of $d$ needed to calculate $P_i$ from Eq.(15) were calculated using the following semiempirical relation $^{17,18}$:

$$d^{5/2} = \frac{1}{7.21 \times 10^{15}} V^{1/4} \frac{1}{T^{5/4}}$$

where $\gamma$ (N.m$^{-1}$) is surface tension and $T_C$ (in Kelvin) is critical temperature. Surface tension of liquids or their mixtures is related to speed of sound through the relation $^{17-20}$:

$$\gamma = 6.3 \times 10^{-4} \rho u^{3/2}$$

where $\rho$ (kg/m$^3$) is density and $u$ (m.s$^{-1}$) is speed of sound. $T_C$ of the mixture was obtained from the following additive relation:

$$\frac{1}{T_{C^{(m)}}} = \sum_{i=1}^{2} \frac{\Phi_i}{T_{C^{(i)}}}$$

where $\Phi_i = x_i V_i / \sum_i (x_i V_i)$ is the volume fraction.

**Bloomfield-Dewan theory**

Viscosity of binary liquid mixtures has been studied extensively over the past several decades $^{21,22}$. Several empirical correlations have been proposed to study the deviations in viscosity of liquid mixtures that generally require adjustable parameters. However, the most commonly used equation to predict the viscosity deviation is:

$$\ln \eta = \ln \eta - (x_1 \ln \eta_1 + x_2 \ln \eta_2)$$
In order to calculate \( \ln \eta^E \) theoretically, Bloomfield and Dewan proposed an equation that does not require any adjustable parameters and which correlates viscosity of the mixture with the thermodynamic properties of pure components. This theory is based on free volume and absolute reaction rate concepts, as well as Flory equation without any numerical adjustment. The Bloomfield-Dewan equation is given as:

\[
\ln \eta^E_{th} = \ln \eta_G + \ln \eta_{fv} = G^E / RT + \ln \eta_{fv}
\]  

By splitting \( G^E \) into enthalpy and entropy contributions we get,

\[
\ln \eta^E_{th} = - H^E / RT + S^E / R + \left[ \frac{1}{p^V - 1} \left( \sum_{i=1}^{2} x_i \frac{1}{p^V - 1} \right) \right]
\]

In order to calculate \( \ln \eta^E_{th} \), the experimental \( H^E \) values were taken from Grolier et al. and the values of \( S^E \) have been calculated from Eq.(13). The free volume contribution to \( \ln \eta^E \) was then calculated in the usual manner from Flory theory.

Using the theory of Eyring, we have calculated the excess molar Gibbs energy of activation for the
Table 4 — Calculated values of $H^E$, $G^E$ and $\partial F^E/\partial T$ for the binary mixtures of 1-CNP with monocyclic aromatics at near equimolar compositions

<table>
<thead>
<tr>
<th>1-CNP +</th>
<th>$x_1$</th>
<th>$H^E$ (J/mol)</th>
<th>$G^E$ (J/mol)</th>
<th>$10^9 \partial F^E/\partial T$ (10^-6 m^3 mol^-1 K^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.5035</td>
<td>323.7</td>
<td>0.896</td>
<td></td>
</tr>
<tr>
<td>Methylbenzene</td>
<td>0.4962</td>
<td>129.5</td>
<td>-1.339</td>
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</tr>
<tr>
<td>1,4-Dimethylbenzene</td>
<td>0.5970</td>
<td>183.8</td>
<td>-1.316</td>
<td></td>
</tr>
<tr>
<td>1,3,5-Trimethylbenzene</td>
<td>0.4984</td>
<td>-39.7</td>
<td>-1.721</td>
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</tr>
<tr>
<td>Methoxybenzene</td>
<td>0.4997</td>
<td>-39.43</td>
<td>-0.279</td>
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</table>

Fig. 3 — Excess internal pressure vs volume fraction at 298.15K for the mixtures of 1-CNP + (O) benzene, 1-CNP + (A) methylbenzene, 1-CNP + (O) 1,4-dimethylbenzene, 1-CNP + (O) 1,3,5-trimethylbenzene and 1-CNP + (V) methoxybenzene.

viscous flow, $G^E$ as:

$$G^E = RT(\ln \eta^V - x_1 \ln \eta_1 V_1 - x_2 \ln \eta_2 V_2) \quad \ldots (23)$$

where $\eta$ and $V$ are respectively, the viscosity and molar volume of the mixture; $\eta_i$ and $V_i$ represent the respective quantities of component $i$ in the mixture and $RT$ has the usual meaning. It may be noted that $G^E$ is a kinetic energy barrier impeding the attainment of the minimum level of a free energy corresponding to thermodynamic equilibrium. However, it is possible to split this contribution between enthalpy or entropy, i.e., $H^E$ or $S^E$ which could be obtained from the temperature dependence of $G^E$. Such $H^E$ or $S^E$ values referring to activation energy (kinetics) cannot be fundamentally replaced by $H^E$ or $S^E$ obtained from thermodynamic equilibrium (discussed earlier).

Benson-Kiyohara theory

Ultrasound data of the mixtures have been used to calculate excess isothermal compressibility, $k_s^E$ and deviations in isentropic compressibility, $k_s^E$. The values of $k_s^E$ have been calculated from Benson-Kiyohara equation using:

$$k_s^E = k_s^{\max} - k_s^{\text{ideal}} \quad \ldots (24)$$

Here, the ideal isentropic compressibility term was computed using the relation:

$$k_s^{\text{ideal}} = k_s^{\text{ideal}} \Phi_1 + k_s^{\text{ideal}} \Phi_2$$

$$+ T \left\{ \Phi_1 V_1 \frac{\alpha_1^2}{C_{p1}} + \Phi_2 V_2 \frac{\alpha_2^2}{C_{p2}} - \frac{V \text{ideal} (\alpha_{\text{ideal}})^2}{C_p^{\text{ideal}}} \right\} \quad \ldots (25)$$

The values of $C_p$ for the individual components of the mixtures are taken from the work of Riddick et al\textsuperscript{27}. In the absence of $C_p$ data for mixtures of 1-CNP
Table 5 — Experimental and computed values of $\ln \eta^f$ Bloomfield-Dewan equation at 298.15 K for near equimolar compositions

<table>
<thead>
<tr>
<th>1-CN with</th>
<th>$\ln \eta_{th}$</th>
<th>$\ln \eta_S$</th>
<th>$\ln \eta_I$</th>
<th>$\ln \eta^f_{th}$</th>
<th>$\ln \eta^f_{exp}$</th>
<th>$(\ln \eta^f_{exp} - \ln \eta^f_{th})$</th>
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</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>-0.859</td>
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<td>Methylenebenzene</td>
<td>-0.588</td>
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<td>0.075</td>
<td>-0.550</td>
<td>-0.016</td>
<td>0.534</td>
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<td>1,4-Dimethylnaphthene</td>
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<td>1,3,5-Trimethylnaphthene</td>
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Fig. 5 — Excess molar Gibbs energy of activation of flow vs mole fraction at 298.15 K for the same mixtures as presented in Fig.3.

Fig. 6 — Excess isentropic compressibility calculated from Benson-Kiyohara theory at 298.15 K for the same mixtures with the symbols as in Fig. 5.

If benzene, the following additive relation was used:

$$C_p = x_1 C_{p_1} + x_2 C_{p_2}$$

The individual component $C_p$ data were taken from Table 1.

**Isothermal compressibility from Flory theory**

The experimental value of $k_I$ as given by Eq.(8) to calculate the deviation in isothermal compressibility, $k_{T}^{E}$ may be expressed as:

$$k_{T}^{E} = k_{T}^{\text{max}} - k_{T}^{\text{ideal}}$$

where the $k_{T}^{\text{max}}$ and $k_{T}^{\text{ideal}}$ terms are computed from Eq.(8). The term $k_{T}^{\text{ideal}}$ is calculated as:

$$k_{T}^{\text{ideal}} = \phi_1 k_{T_1}^{\text{ideal}} + \phi_2 k_{T_2}^{\text{ideal}}$$

We have also attempted to compute $k_T$ from Flory theory. A survey of the literature indicates that very few attempts have been made to predict $k_T^E$ using Flory theory as given below.

**Prigogine-Saraga theory**

In order to judge the validity of speed of sound data, we have also computed theoretically the values of $u$ from Prigogine-Saraga theory by rearranging Eq.(17) as:

$$u = \left[ \gamma^{10/6.3} \rho \right]^{2/3}$$

where $\gamma$ is surface tension. In order to calculate $u$ in m.s$^{-1}$, the input values of $\gamma$ and $\rho$ were taken in the c.g.s. units.

$$\gamma = \gamma^* \tilde{\gamma}$$

where $\gamma^*$ and $\tilde{\gamma}$ are the characteristic and reduced surface tension, respectively. According to Patterson
Table 6—Estimated parameters of excess functions for the binary mixtures

<table>
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<th>Function</th>
<th>Temp/K</th>
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<th>$A_1$</th>
<th>$A_2$</th>
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<td>$\ln T^{E}/(mPa.s)$</td>
<td>298.15</td>
<td>0.069</td>
<td>0.0974</td>
<td>0.028</td>
<td>0.008</td>
</tr>
<tr>
<td>$G^{E}/(J.mol^{-1})$</td>
<td>298.15</td>
<td>248</td>
<td>254</td>
<td>81.1</td>
<td>0.101</td>
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<tr>
<td>$10^6. P_i^{E}/(TPa)$</td>
<td>298.15</td>
<td>-0.872</td>
<td>-0.686</td>
<td>0.384</td>
<td>0.030</td>
</tr>
<tr>
<td>$k_i^{E}/(TPa^{-1})$</td>
<td>298.15</td>
<td>76.0</td>
<td>18.6</td>
<td>23.26</td>
<td>0.048</td>
</tr>
</tbody>
</table>

1-Chloronaphthalene(1) + Benzene(2)

<table>
<thead>
<tr>
<th>Function</th>
<th>Temp/K</th>
<th>$A_0$</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T^{E}/10^{6}$ (m$^3$.mol$^{-1}$)</td>
<td>298.15</td>
<td>-1.40</td>
<td>-0.308</td>
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<td>0.013</td>
</tr>
<tr>
<td>$\ln T^{E}/(mPa.s)$</td>
<td>298.15</td>
<td>-0.244</td>
<td>0.105</td>
<td>-0.027</td>
<td>0.005</td>
</tr>
<tr>
<td>$G^{E}/(J.mol^{-1})$</td>
<td>298.15</td>
<td>-619.5</td>
<td>253.6</td>
<td>87</td>
<td>1.11</td>
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<tr>
<td>$10^6. P_i^{E}/(TPa)$</td>
<td>298.15</td>
<td>-0.258</td>
<td>0.120</td>
<td>-0.457</td>
<td>0.014</td>
</tr>
<tr>
<td>$k_i^{E}/(TPa^{-1})$</td>
<td>298.15</td>
<td>-137.7</td>
<td>-39.5</td>
<td>8.17</td>
<td>0.455</td>
</tr>
</tbody>
</table>

Results and Discussion

The excess molar volumes have been calculated from the experimental densities of liquids and liquid mixtures using the equation,

$$V^E = V_m - V_1 x_1 - V_2 x_2$$

where $V_m$ is molar volume of binary mixture calculated as $V_m = (M_1 x_1 + M_2 x_2) / \rho_m$; $\rho_m$ is mixture density; and $V_1 (= M_1 / \rho_1)$ and $V_2 (= M_2 / \rho_2)$ are the molar volumes of components 1 and 2; $M_1$, $\rho_1$, and $M_2$, $\rho_2$ are the molecular weights and densities of components 1 and 2 respectively. The equimolar experimental $V^E$ values are compared with the $V^E$ values calculated from Flory and PFP theories at 298.15 K in Table 3. It is observed that in all the cases, the $V^E$ values are negative and compare well with the PFP $V^E$ values rather than with the Flory $V^E$ values. However, the results presented in Fig.1 are
compared for only two typical mixtures, viz., 1-CNP + benzene and 298.15 K. Similar data are presented in Fig. 2 for the mixture of 1-CNP + 1,3,5-trimethylbenzene and 1-CNP + methoxybenzene at 298.15 K. It can be seen that the values of thermal expansivity, $\alpha$ and isothermal compressibility, $k_i$ for 1-CNP are lower than those for other liquids (Table 1). Thus, when it is mixed with aromatic liquids having increasing number of methyl-groups, the binary mixtures exhibit large free volume effects. This explains the observed increased values of $V^E$ with increasing number of methyl groups on benzene moiety. The calculated values of $H^E$ and $G^E$ for all the mixtures except those of 1-CNP + 1,3,5-trimethylbenzene or 1-CNP + methoxybenzene are positive suggesting order creation in these mixtures. This is attributed to (i) $\pi-\pi$ interactions between 1-CNP and monocyclic aromatics (except those containing 1,3,5-trimethylbenzene or methoxybenzene). This is further supported by the fact that the values of second order mixing quantities, i.e., $\partial V^E/\partial T$ are negative for all the mixtures (Table 4) suggesting that there is a short-range orientational order effect between 1-CNP and the monocyclic aromatic molecules. When two plate like molecules are mixed, the order is created due to a regular alignment, but such an order might possibly be destroyed whenever the bulky methoxy group is present (as in methoxybenzene).

The PFP contribution terms due to interactional, free volume and internal pressure along with $\theta_3$ and $X_{12}$ terms are also included in Table 3. In the original PFP theory, the interactional term is positive in the absence of H-bond and other specific interactions. However, for the mixtures of 1-CNP + 1,3,5-trimethylbenzene or 1-CNP + methoxybenzene, the PFP interactional contribution terms are negative. Since the interactional term is dominant in $H^E$, the negative values of $H^E$ for these mixtures are responsible for giving the negative values of the interactional terms. Similarly, the $G^E$ terms follow the same signs as those of $H^E$ as shown in Table 4. However, the free volume terms are positive in all the cases, whereas the internal pressure contribution term is negative in all the mixtures except 1-CNP + methoxybenzene. This further supports the fact that the internal pressure ($P^{*}$) term often dominates $V^E$, particularly if one of the components has a higher $P^{*}$ value and lower $\alpha$ than the other. This situation leads to negative $V^E$ with negative $I^E$. This is indeed the case for 1-CNP + methoxybenzene system. It may further be noted that even the values of $X_{12}$ for the mixtures 1-CNP + 1,3,5-trimethylbenzene and 1-CNP + methoxybenzene are negative which parallel the negative values of internal pressure contribution observed for these mixtures. In view of the nonavailability of $H^E$ data for the present mixtures, the $X_{12}$ values have been calculated using the experimental $V^E$ data at 298.15 K as:

$$X_{12} = \frac{1}{(\phi_1 \phi_2 (X_{12}))}
\left[ \sum \phi_i R_i \left( \bar{T}(X_{12}) - \bar{T}_i(X_{12}) \right) \right]
\quad \ldots (35)$$

The values of $X_{12}$ thus calculated are positive for all the mixtures except those of 1-CNP + 1,3,5-trimethylbenzene and 1-CNP + methoxybenzene mixtures (Table 3).

The values of excess internal pressure, $P^E_1$, calculated from the difference between the mixture and individual components using Eqs (15-18) based on volume fraction, $\Phi_i$, of 1-CNP are presented in Fig. 3. It is found that for 1-CNP + 1,3,5-trimethylbenzene, the $P^E_1$ values are positive while the negative values are observed for the remaining mixtures except 1-CNP + 1,4-dimethylbenzene for which $P^E_1$ values are almost independent of mixture composition. Such negative values indicate that the repulsive forces between the interacting molecules
have a predominant effect for those mixtures exhibiting positive values of $P_t^E$ and thus, indicating that the attractive forces are greater than the repulsive interactions. The excess internal pressure decreases considerably for mixtures of 1-CNP + benzene as evidenced by a large negative value when compared to 1-CNP + 1,3,5-trimethylbenzene, for which the $P_t^E$ values are positive.

The calculated values of $\ln \eta^E$ from the Bloomfield and Dewan equation are compared with those of the experimentally calculated values in Table 5. The enthalpy, entropy and free volume contribution terms, viz., $\ln \eta_{H}$, $\ln \eta_{S}$ and $\ln \eta_{F}$ to viscosity are also listed. The differences between the experimental and predicted values of $\ln \eta^E$ for all the mixtures are quite larger than that for 1-CNP + methoxybenzene. However, for the mixtures the signs of the experimentally calculated and theoretically predicted values of $\ln \eta^E$ are identical except in case of 1-CNP + benzene mixture. Similarly, the experimental and theoretical $\ln \eta^E$ curves for 1-CNP + methoxybenzene and 1-CNP + 1,3,5-trimethylbenzene are presented in Fig. 4. The agreement between theory and experiment is again poor. Such differences between theoretical and experimental quantities are attributed to: (i) the over estimation of the entropy contribution, i.e., $S^F/R$ term determined from the free volume difference and (ii) use of the calculated $H^F$ data instead of experimental measurements.

The results of free energy of activation of flow, $G^F$ are presented in Fig. 5 and these curves do not exhibit any systematic dependence on the size of the aromatic molecules in the binary mixtures. The plots of $k_S^E$ calculated from Eq. (24) are presented in Fig. 6. Higher negative values are observed for all the binaries except 1-CNP + methoxybenzene (for which there is no dramatic dependence of $k_S^E$ on $\Phi_j$). In Fig. 7 are compared the predicted values of $k_t^E$ from Benson-Kiyohara theory with those computed from the experimental data for a few representative systems, viz., 1-CNP + benzene, 1-CNP + 1,4-dimethylbenzene and 1-CNP + 1,3,5-trimethylbenzene. In all the cases, the $k_t^E$ values are negative and larger deviations are observed between the predicted and experimental curves for 1-CNP+benzene when compared to 1-CNP+1,4-dimethylbenzene or 1-CNP + 1,3,5-trimethylbenzene.

The values of excess functions viz., $V^E$, $\ln \eta^E$, $G^E$, $P_t^E$ and $k_t^E$ have been fitted to Redlich Kister Equation (32) of the type:

$$V^E = C_1 C_2 \sum_{j=1}^{k-3} A_{p4} (C_2 - C_1)^j$$

(36)

to estimate the parameter values of $A_0$, $A_1$, $A_2$ along with the standard deviations, $\sigma$ and these are compiled in Table 6.

In conclusion, the present approach is an attempt to understand the agreement between the well established theoretical predictions and the experimentally calculated quantities which are frequently used in the study of binary liquid mixtures. The results presented here will be useful to gain a better understanding of the mixing phenomena in binary mixtures.

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References

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