Viscometric studies of molecular interactions in binary liquid mixtures of dichloromethane and some nonpolar solvents

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Viscosities of the polar molecule, dichloromethane in mixtures with nonpolar solvents cyclohexane, benzene, p-xylene and mesitylene have been measured at two different temperatures 293.15 K and 303.15 K. The viscosities of binary liquid mixtures prepared with cyclohexane show appreciable negative deviation from rectilinear dependence on mole fraction of dichloromethane. This deviation decreases in the case of benzene and p-xylene and becomes positive for the binary mixture with mesitylene. The deviation is positive even for the binary mixture with p-xylene at 303.15 K. An attempt has been made to correlate the deviation of viscosity from the rectilinear dependence, the parameters \( d \) of Grunberg-Nissan equation and \( C \) of Hind-McLaughlin-Ubbelohde equation and the interchange energy \( W_{\text{mix}} \) with the degree of interaction. It is found that the value of \( C \) is more consistent than the value of \( d \).

The importance of dipole-induced dipole interactions and steric factors in the formation of molecular complex between a polar and a nonpolar molecules has been emphasized by NMR studies. The contentions have been supported by the dielectric studies. The molecular interactions in binary liquid mixtures have also been studied on the basis of viscosity measurements. Nigam et al. have critically examined Rowlinson-Sutton theory of binary mixtures based on orientation dependent potential in the light of excess thermodynamic properties for the binary mixtures of disubstituted methane with some hydrocarbons. However, monosubstituted polar molecules have generally been used for such studies. In this note we have employed viscosity measurements for the study of molecular interactions in binary liquid mixtures consisting of the disubstituted polar molecule, dichloromethane and nonpolar aromatic solvents with different polarisabilities and steric environment, viz. benzene, p-xylene and mesitylene. Studies have also been made using cyclohexane as inert solvent to provide a reference point for the assessment of the interactions.

Experimental

The polar molecule employed was dichloromethane (Qualigens, Glindia, purity better than 99%) and the nonpolar solvents were cyclohexane (TOMAC BEKEP, London, purity 99.7%), benzene (Sarabhai, purity 99.5%), p-xylene (BDH, England, purity 99.5%) and mesitylene (Fluka, purity 99%). Viscosities of the binary mixtures were determined with a Chuan-Fuoss viscometer correct to \( \pm 0.001 \) centipoise. Densities of the mixtures were measured using a pycnometer correct to \( \pm 0.0001 \) g cm\(^{-3}\). Precautions were taken to avoid losses by evaporation. Kinematic viscosity, \( \nu \), was obtained from the two term equation,

\[
\nu = \frac{\eta}{\rho} = \frac{a}{t} - \frac{b}{t}
\]

where \( \eta \) and \( \rho \) are shear viscosity and density respectively of the liquid and \( t \) is the flow time in seconds, \( a \) and \( b \) are the characteristic constants of the viscometer. The viscometer was calibrated by measuring the time of flow for liquids of known viscosity and the constants \( a \) and \( b \) were found to be 0.0000277 and 0.0343291 at 293.15 K and 0.0000272 and 0.0314711 at 303.15 K respectively. All the measurements were made in a toluene-regulated thermostat controlled to \( \pm 0.1 \) K.

Values of parameter \( d \) were calculated using the Grunberg-Nissan equation,

\[
\ln \eta_{12} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d
\]

where \( \eta_1 \) and \( \eta_2 \) are the viscosities and \( x_1 \) and \( x_2 \) are the mole fractions of the component liquids 1 and 2 respectively. \( \eta_{12} \) is the viscosity of the binary mixture. The values of \( d \) show a significant percentage variation over the entire composition range. In view of the above and the suggestion made by Palit et al. to use Grunberg-Nissan equation cautiously it was thought necessary to
examine the relative suitability of another equation proposed by Hind-McLaughlin-Ubbelohde as,

\[ \eta_{12} = x_1^2 \eta_1 + x_2^2 \eta_2 + 2x_1 x_2 C \]  

where \( C \) is an interaction parameter. The interchange energy (\( W_{\text{int}} \)) was also evaluated using viscosity data employing equation,

\[ W_{\text{int}} = \frac{2.30258 RT}{A_1 x_1 x_2 (x_2 + (A_2/A_1) x_1)} \]

where the terms have their usual meaning.

Results and discussion

The values of the viscosities (\( \eta_{12} \)) with the mole fractions of dichloromethane for all binary mixtures studied at temperatures 293.15 K and 303.15 K are shown in Figs 1 to 4. Excess viscosities (\( \Delta \eta^{E} = \eta_{12} - x_1 \eta_1 - x_2 \eta_2 \)), the parameters \( d \) and \( C \) and the interchange energy (\( W_{\text{int}} \)) for the binary mixtures studied at 293.15 K and 303.15 K as a function of composition are reported in Tables 1 and 2 respectively. A perusal of Fig. 1 shows that there is an appreciable negative deviation from the rectilinear dependence of viscosity on the mole fraction of the polar molecule containing cyclohexane. This negative deviation is sufficiently reduced when benzene is the non-polar solvent in the mixture.

It appears that in the case of polar molecule cyclohexane, the binary liquid mixtures are less viscous. This is quite likely in view of the known tendency of dichloromethane to associate, the effect of which is reduced on dilution with inert cyclohexane. However, polar molecule, aromatic solvent mixture of a certain composition, becomes more viscous than the binary mixture with cyclohexane in view of enhanced intermolecular forces in the mixture. The enhancement could be due to dipole-induced dipole interaction proportional to the polarisability of the aromatic molecules. As \( p \)-xylene and mesitylene are more polarisable than benzene, increased interactions of polar molecule with the former two aromatic solvents and associated increase in the mixture viscosities are expected.

Cyclohexane, with its known flexible structure, is quite likely to reduce mixture viscosities when present in a binary mixture with a polar molecule as compared to the rigid aromatic hydrocarbons. Steric overcrowding on the aromatic hydrocarbon
Table 1—Excess viscosities ($\Delta \eta^\text{E}$), $d$ and $C$ values and inter-change energy ($W_{\text{visc}}$) with mole fractions of dichloromethane ($x_1$) for the binary mixtures of dichloromethane + nonpolar solvents at 293.15 K

<table>
<thead>
<tr>
<th>$x_1$</th>
<th>$\Delta \eta^\text{E}$ (CP)</th>
<th>$d$</th>
<th>$C$</th>
<th>$W_{\text{visc}}$ (k cal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>0.0986</td>
<td>-0.039</td>
<td>-0.26</td>
<td>0.48</td>
</tr>
<tr>
<td>0.0127</td>
<td>0.1979</td>
<td>-0.067</td>
<td>-0.25</td>
<td>0.49</td>
</tr>
<tr>
<td>0.0254</td>
<td>0.2980</td>
<td>-0.100</td>
<td>-0.35</td>
<td>0.47</td>
</tr>
<tr>
<td>0.0381</td>
<td>0.4011</td>
<td>-0.106</td>
<td>-0.35</td>
<td>0.48</td>
</tr>
<tr>
<td>0.0508</td>
<td>0.5016</td>
<td>-0.107</td>
<td>-0.36</td>
<td>0.49</td>
</tr>
<tr>
<td>0.0635</td>
<td>0.5987</td>
<td>-0.107</td>
<td>-0.43</td>
<td>0.48</td>
</tr>
<tr>
<td>0.0762</td>
<td>0.6999</td>
<td>-0.104</td>
<td>-0.57</td>
<td>0.46</td>
</tr>
<tr>
<td>0.0889</td>
<td>0.7978</td>
<td>-0.086</td>
<td>-0.70</td>
<td>0.43</td>
</tr>
<tr>
<td>0.1000</td>
<td>0.9005</td>
<td>-0.040</td>
<td>-0.57</td>
<td>0.48</td>
</tr>
<tr>
<td>0.1158</td>
<td>1.0000</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2—Excess viscosities ($\Delta \eta^\text{E}$), $d$ and $C$ values and inter-change energy ($W_{\text{visc}}$) with mole fractions of dichloromethane ($x_1$) for the binary mixtures of dichloromethane + nonpolar solvents at 303.15 K

<table>
<thead>
<tr>
<th>$x_1$</th>
<th>$\Delta \eta^\text{E}$ (CP)</th>
<th>$d$</th>
<th>$C$</th>
<th>$W_{\text{visc}}$ (k cal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>0.0963</td>
<td>-0.023</td>
<td>-0.12</td>
<td>0.48</td>
</tr>
<tr>
<td>0.0127</td>
<td>0.1940</td>
<td>-0.035</td>
<td>-0.08</td>
<td>0.49</td>
</tr>
<tr>
<td>0.0254</td>
<td>0.2932</td>
<td>-0.045</td>
<td>-0.08</td>
<td>0.50</td>
</tr>
<tr>
<td>0.0381</td>
<td>0.3983</td>
<td>-0.052</td>
<td>-0.09</td>
<td>0.50</td>
</tr>
<tr>
<td>0.0508</td>
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<td>-0.052</td>
<td>-0.09</td>
<td>0.50</td>
</tr>
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<td>0.0635</td>
<td>0.5975</td>
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<td>0.50</td>
</tr>
<tr>
<td>0.0762</td>
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<td>-0.044</td>
<td>-0.13</td>
<td>0.50</td>
</tr>
<tr>
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<td>-0.12</td>
<td>0.51</td>
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<tr>
<td>0.1000</td>
<td>0.8954</td>
<td>-0.022</td>
<td>-0.16</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Dichloromethane ($x_1$) + Cyclohexane ($x_2$)
due to methyl substitution would make the process still more difficult, i.e. will enhance the viscosity which is in line with experimental observations reported here.

In an earlier publication\(^1\) \(d\) values were said to be indicative of specific interactions; large positive \(d\) values indicate strong specific interactions while small positive values indicate weak interactions, and largely negative values indicate no specific interactions.

It is evident from Table 1 that the \(d\) values are largely negative with cyclohexane, less negative with benzene and slightly negative with \(p\)-xylene and positive with mesitylene. In view of the above it seems more appropriate to regard the parameter \(d\) as a measure of the resultant interaction, rather than to associate different range of \(d\) values with different types of exclusive interactions. Large negative \(d\) values for binary mixtures with component cyclohexane indicate the existence of weak interactions due mainly to dispersion forces. Increased (less negative) \(d\) values for mixtures of polar molecule with benzene indicate stronger interaction due to appreciable dipole-induced dipole interaction. Still higher \(d\) values for the mixtures prepared with \(p\)-xylene and a positive \(d\) value with mesitylene seem to be due to enhanced dipole-induced dipole interaction on account of higher polarisability of methyl substituted benzene.

The parameter \(C\) attributes to unlike pair interaction. It is evident from Tables 1 and 2 that the percentage variation of \(C\) values is smaller as compared to \(d\) values. It shows that the Hind-McLaughlin-Ubbelohde equation expresses the mixture viscosity better than the Grunberg-Nissan equation for the systems studied.

A perusal of the Table 1 shows that the \(W_{visc}\) values are highly positive with cyclohexane, less positive with benzene, lesser positive with \(p\)-xylene and negative with mesitylene. This again suggests the graded behaviour of the interactions.

The values of interchange energy, \(W_{interchange}\) as obtained by the viscosity measurement seem to fall in line with the values of heat of mixing anticipated on the basis of the degree of interaction in various mixtures. The interaction between a pair of polar molecule dichloromethane is usually expected to be higher than that between unlike pairs of molecules (dichloromethane and cyclohexane). Therefore, it is obvious that the formation of such a mixture would be accompanied by the absorption of heat i.e. large positive intermolecular energy.

When the strength of the interactions between unlike pairs of molecules (dichloromethane and non-polar aromatic molecule) becomes comparable to that between the like pairs of molecules, the magnitude of the interchange energy is expected to be small. The negative values of \(W_{visc}\) for the binary mixture of dichloromethane with mesitylene at 293.15 \(K\) indicate the evolution of heat clearly showing that the attractive forces between the unlike pairs of molecules in such mixtures have overtaken the interaction between the like pairs of molecules. Thus the values of \(W_{visc}\) also give the similar conclusion as that obtained by the \(d\) values.

The deviation in the viscosity of the mixture from rectilinear dependence on the mole fraction of the polar molecule usually diminishes with temperature which is obvious in view of diminished intermolecular interactions at higher temperature. However, the deviation becomes positive in the binary mixtures of dichloromethane with \(p\)-xylene and mesitylene.

References
4 Yadava R R & Yadava S S, Indian J Chem, 16A (1979) 120.