Excess molar volumes and viscosities of binary mixtures of diethylene glycol dibutyl ether with chloroalkanes at 298.15 K

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Excess molar volumes ($V_m^E$) and dynamic viscosities ($\eta$) for mixtures of diethylene glycol dibutyl ether + dichloromethane, + trichloromethane, and + tetrachloromethane have been determined as a function of composition at 298.15 K and atmospheric pressure. The excess molar volumes $V_m^E$ are all negative over the whole composition range. The viscosity data have been correlated by the methods of Kendall and Monroe, Grunberg and Nissan, Tamura and Kurata, Hind, Katti and Chandhary, and of McAllister. The deviations in viscosities ($\Delta\eta$) and excess energies of activation ($\Delta G^E$) for viscous flow have been calculated from the experimental results. These results have been discussed in terms of dipole–dipole interactions between diethylene glycol dibutyl ether and chloroalkanes and magnitudes of interactions decreasing with the dipole character of the molecule. A short comparative study with results for mixtures with polyethers or alkoxyethanols and chloroalkanes is also presented.

In continuation of our previous studies on binary mixtures containing polyethers or alkoxyethanols and chloroalkanes, we report herein the excess molar volumes ($V_m^E$), viscosity deviations ($\Delta\eta$) and excess energies of activation ($\Delta G^E$) for viscous flow for binary mixtures of diethylene glycol dibutyl ether with dichloromethane (DCM), trichloromethane (TCM) and tetrachloromethane (TC), over the whole mole fraction range at 298.15 K and atmospheric pressure. Excess properties of binary mixtures containing chloroalkanes have previously been studied by some authors. The present study was, therefore, undertaken in order to compare the excess molar volumes and deviations in viscosity of diethylene glycol dibutyl ether + chloroalkanes with those of our results for diethylene glycol diethyl ether + chloroalkanes by enlarging of the alkyl group, that is, by the addition of a C$_2$H$_4$ unit, for species with a common polar head group. It is felt that a clear understanding of molecular interactions in (polyether + chloroalkane) mixtures can be obtained by extending the measurements to some other polyethers. An attempt is also made to rationalize the results by collecting the data on (polyethers or alkoxyethanols + chloroalkane) mixtures.

Materials and Methods

Materials were of the same origin and purity as used in earlier studies. Diethylene glycol dibutyl ether (Merck–Schuchardt, FRG, GC > 98 %) was dried over FeSO$_4$ (AR, BDH) and then fractionally distilled twice before use under reduced nitrogen pressure. Prior to measurements, all liquids were stored in contact with 0.4 nm molecular sieves to reduce water content, and were partially degassed under vacuum. Densities of pure solvents were measured with a bicipillary pycnometer. The pycnometer was calibrated with doubly distilled water and benzene at 298.15 K and atmospheric pressure. The sensitivity of the pycnometer corresponded to a precision in density of 1 $\times$ 10$^{-2}$ kg m$^{-3}$. The reproducibility of the density estimated was found to be 1 $\times$ 10$^{-3}$ kg m$^{-3}$. Diethylene glycol dibutyl ether, di-, tri-, and tetrachloromethanes at 298.15 K had densities of 878.5 [lit. 879.5 (ref. 12); 878.30 (ref. 13)], 1316.3 [lit. 1316.78 (ref. 12); 1316.2 (ref. 14); 1316.8 (ref. 15)], 1479.4 [lit. 1479.70 (ref. 12); 1479.1 (ref. 14); 1472.7 (ref. 16)], 1584.3 [lit. 1584.36 (ref. 12); 1584.3 (ref. 14); 1584.3 (ref. 15)] kg m$^{-3}$ and viscosities 2.160, 0.406 [lit. 0.4043 (ref. 12); 0.410 (ref. 14)], 0.532 [lit. 0.5357 (ref. 12); 0.537 (ref. 14); 0.5357 (ref. 16)], 0.905 [lit. 0.9004 (ref. 12); 0.900 (ref. 14)] mPa s, respectively.
The measurements of excess molar volumes were carried out by a continuous dilution dilatometer in a way similar to that described by Dickinson et al.\textsuperscript{17}. Details of its calibration, experimental setup and operational procedures have been described elsewhere\textsuperscript{18,19}. The dilatometer was clamped vertically into the water bath. The mercury meniscus as well as the reference mark, were measured with a cathetometer that could read correctly to within 0.1 mm. The results for excess molar volumes are reproducible to $\pm 0.003 \times 10^{-6}$ m$^3$/mol$^{-1}$. Each run covered just over half of the mole fraction range, giving an overlap between two runs. The mole fraction of each mixture was obtained to an accuracy of $1 \times 10^{-4}$ from the measured apparent mass of one of the components. All apparent masses were corrected for buoyancy. Conversion to molar quantities was based on the relative atomic mass table of 1985 issued by IUPAC\textsuperscript{20}.

The kinematic viscosities $\eta (=\eta/\rho)$ in both the pure liquids and their mixtures were measured at 298.15 K and at atmospheric pressure using an Ubbelohde suspended level viscometer\textsuperscript{21}. The viscometer was calibrated so as to determine the two constants $A$ and $B$ in the equation $\eta/\rho = At - Bt^2$, obtained by measuring the flow time $t$ with thrice distilled water and twice distilled benzene and cyclohexane. The details of the apparatus and procedure were described previously\textsuperscript{22,23}. The viscometer was filled with liquid or liquid mixtures and its limbs were closed with teflon caps taking due precautions to minimize the evaporation losses. An average of four or five sets of flow times were taken for each liquid and liquid mixtures. The flow-time measurements were made with an electronic stopwatch having a precision of $\pm 0.01$s. The caps of the limbs were removed during the measurements of flow time. After multiplication by density, the dynamic viscosity ($\eta$) was deduced with a relative error of $\pm 0.003$ mPa s. The performance of the viscometer was assessed by measuring and comparing the viscosities of the pure components with the values reported in the literature\textsuperscript{22,23}. A thermostatically controlled, well-stirred water bath whose temperature was controlled to $\pm 0.01$K was used for all the measurements.

Results and Discussion

Results of measurements of excess molar volumes for diethylene glycol dibutyl ether (1) + dichloromethane(2), + trichloromethane(2), and + tetrachloromethane(2) at number of mole fractions at 298.15 K and atmospheric pressure are graphically represented in Fig. 1. For compact and smooth representation, the experimental values of $\eta$ were fitted to a polynomial function in the form

$$\eta = \sum_{i=1} a_i x_i^{n-1}$$

The value of the coefficients $a_i$ and standard deviations $\sigma$ are summarized in Table I. From the measured values of excess molar volumes, densities of liquid mixtures were calculated using the following equation

$$\rho = (x_1 M_1 + x_2 M_2)/(V_{m1}^{\text{E}} + x_1 V_1^{\text{V}} + x_2 V_2^{\text{V}})$$

where $M_1$ and $M_2$ represent molar masses and $V_i^{\text{V}}$ is the molar volume of the $i$th component. The accuracy in $\rho$ due to the estimated accuracy in excess molar volume ($\pm 0.003 \times 10^{-6}$ m$^3$/mol$^{-1}$) is $1 \times 10^{-1}$ kg m$^{-3}$.

The deviations of the viscosities from the ideal mixture values can be calculated from the following relationship\textsuperscript{25,26}.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Fig_1.png}
\caption{Experimental excess molar volumes ($V_{m1}^{\text{E}}$) for $x_1$C$_2$H$_4$OCH$_2$CH$_2$OCH$_2$H + $x_2$ CH$_2$Cl$_2$, O$_2$ + $x_2$ CHCl$_3$, A$_2$ + $x_2$ CCl$_4$. The continuous curves were calculated from Eq. (5).}
\end{figure}
\[ \Delta \ln \eta = \ln \eta - (x_1 \ln \eta_1 + x_2 \ln \eta_2) \] ... (3)

where \( x_1 \) and \( x_2 \) are the mole fractions, \( \eta \) is the dynamic viscosity of the mixtures, and \( \eta_1 \) and \( \eta_2 \) are the viscosities of components 1 and 2.

On the basis of the theory of absolute reaction rates\(^2\), the excess Gibbs free energies of activation for viscous flow were obtained from this expression

\[ \Delta G^{E} = RT \left[ \ln (\eta V) - x_1 \ln (\eta_1 V_1^s) - x_2 \ln (\eta_2 V_2^s) \right] \] ... (4)

where \( V = \sum x_i M_i / \rho \), \( R \) and \( T \) have their usual meaning.

The values of \( V_{\text{mix}}^E \), \( \Delta \ln \eta \), and \( \Delta G^{E} \) for each mixtures were fitted to a Redlich-Kister\(^2\) polynomial equation of the type

\[ F = x_1 x_2 \sum_{i=1}^{n} a_i (x_1 - x_2)^{i-1} \] ... (5)

where \( a_i \) is the polynomial coefficients and \( m \) is the polynomial degree. The values of the coefficients \( a_i \) obtained by the least-squares method with all points weighted equally are given in Table 2 along with standard deviations \( \sigma \). In each case, the optimum number of coefficients was ascertained from an examination of the variation of the standard deviation with \( m \).

The equation of Kendall and Monroe\(^6\), which has no adjustable parameter, is expressed as

\[ \eta = (x_1 \eta_1^{1/3} + x_2 \eta_2^{1/3})^{3} \] ... (7)

The equations of Grunberg-Nissan, Tamura and Kurata, hind, and Katti and Chaudhary have one adjustable parameter. Grunberg and Nissan provided the following empirical equation containing one adjustable parameter\(^7\). The expression is

\[ \ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \] ... (8)

### Table 1—Coefficients \( a_i \) from Eq. (1) for viscosity \( \eta (\text{mPa} \cdot \text{s}) \) and standard deviation \( \sigma \)

<table>
<thead>
<tr>
<th>( x_1 \text{C}_4\text{H}_4(\text{OCH}_3\text{CH}_2)_2\text{OC}_2\text{H}_5 )</th>
<th>( a_1 )</th>
<th>( a_2 )</th>
<th>( a_3 )</th>
<th>( a_4 )</th>
<th>( a_5 )</th>
<th>( \sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x_2 \text{Cl}_2 \text{H}_2 )</td>
<td>0.397</td>
<td>2.806</td>
<td>0.699</td>
<td>-3.608</td>
<td>1.902</td>
<td>0.005</td>
</tr>
<tr>
<td>( x_2 \text{CHCl}_3 )</td>
<td>0.520</td>
<td>3.583</td>
<td>1.285</td>
<td>-7.069</td>
<td>4.514</td>
<td>0.010</td>
</tr>
<tr>
<td>( x_2 \text{CCl}_4 )</td>
<td>0.893</td>
<td>2.971</td>
<td>-3.108</td>
<td>-2.214</td>
<td>-0.003</td>
<td>0.004</td>
</tr>
</tbody>
</table>

### Table 2—Coefficients \( a_i \) from Eq. (5) and standard deviation \( \sigma \) determined by the method of least-squares

<table>
<thead>
<tr>
<th>( x_1 \text{C}_4\text{H}_4(\text{OCH}_3\text{CH}_2)_2\text{OC}_2\text{H}_5 )</th>
<th>( V_{\text{mix}}^E \times 10^{3} (\text{m}^3 \cdot \text{mol}^{-1}) )</th>
<th>( \Delta \ln \eta (\text{mPa} \cdot \text{s}) )</th>
<th>( \Delta G^{E} (\text{J} \cdot \text{mol}^{-1}) )</th>
<th>( \sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x_2 \text{Cl}_2 \text{H}_2 )</td>
<td>(-2.511 )</td>
<td>(-2.240 )</td>
<td>(7610 )</td>
<td>0.001</td>
</tr>
<tr>
<td>( x_2 \text{CHCl}_3 )</td>
<td>(-4.190 )</td>
<td>(-4.190 )</td>
<td>(7585 )</td>
<td>0.001</td>
</tr>
<tr>
<td>( x_2 \text{CCl}_4 )</td>
<td>(-1.223 )</td>
<td>(1.071 )</td>
<td>(3703 )</td>
<td>0.001</td>
</tr>
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</table>
where $G_{12}$ is a parameter proportional to the interchange energy. Tamura and Kurata developed expression (9) for viscosity of binary mixtures:

$$\eta = x_1 \phi_1 \eta_1 + x_2 \phi_2 \eta_2 + 2(x_1 x_2 \phi_1 \phi_2)^{1/2} T_{12} \ldots \tag{9}$$

where $T_{12}$ is the interaction parameter $\phi_1$ and $\phi_2$ are the volume fractions. Hind et al.\(^1\) suggested Eq. (10)

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2x_1 x_2 H_{12} \ldots \tag{10}$$

where $H_{12}$ is attributed to unlike pair interactions. Katti and Chaudhary\(^2\) developed the Eq. (11)

$$\ln \eta = x_1 \ln(V_1^\eta \eta_1) + x_2 \ln(V_2^\eta \eta_2) + x_1 x_2 W_{ab}/RT \ldots \tag{11}$$

$W_{ab}$ is an adjustable parameter.

McAllister's multi-body interaction model\(^3\) was widely used to correlate kinematic viscosity ($\eta$) data. The two-parameter McAllister equation based on Eyre's theory of absolute reaction rates, taken into account interactions of both like and unlike molecules by a two-dimensional three-body model. The three-body model was defined as

$$\ln \eta = x_1 \ln(V_1^\eta \eta_1) + x_2 \ln(V_2^\eta \eta_2) + x_1 x_2 W_{ab}/RT \ldots \tag{11}$$

where $\eta$ is an adjustable parameter.

In this work, the dynamic viscosity $\eta$ has also been studied for these systems and often yields valuable information relating to the interaction between the molecules. Figure 2 shows that $\eta$ increases with increase in the mole fraction $x_i$ of polyether for all mixtures. From the values of $\eta$, we have calculated $\Delta \ln \eta$ and $\Delta G^\mu$ at 298.15 K as shown in Figs 3 and 4. The positive values of $\Delta \ln \eta$ would imply that the mixture is more viscous than (i) the corresponding ideal mixtures and (ii) the specific interactions, as corroborated by the negative $V_m^E$ and positive $\Delta G^\mu$ values.

The results of the correlating equations (Eqs 7-13) are compiled in Table 3. The values of the different adjustable parameters induced in Eqs (7-13) are reported in Table 3 together with the percentage standard deviations ($\sigma$ %) between the calculated and experimental values. The values of $\sigma$ are in the range.
Fig. 2—Experimental viscosities (η) for \( x_1 \) C\(_4\)H\(_8\)OCH\(_2\)CH\(_2\)OC\(_4\)H\(_8\) + \( x_2 \) CH\(_2\)Cl\(_2\), Q; + \( x_1 \) CHCl\(_3\), \( \Delta \); + \( x_2 \) CCl\(_4\), \( \Box \). The continuous curves were calculated from Eq. (1).

Fig. 3—Experimental viscosity deviations (Δη/η) for \( x_1 \) C\(_4\)H\(_8\)OCH\(_2\)CH\(_2\)OC\(_4\)H\(_8\) + \( x_2 \) CH\(_2\)Cl\(_2\), Q; + \( x_1 \) CHCl\(_3\), \( \Delta \); + \( x_2 \) CCl\(_4\), \( \Box \). The continuous curves were calculated from Eq. (5).

Fig. 4—Excess free energies of activation (\( \Delta G^{\text{F}} \)) for viscous flow for \( x_1 \) C\(_4\)H\(_8\)OCH\(_2\)CH\(_2\)OC\(_4\)H\(_8\) + \( x_2 \) CH\(_2\)Cl\(_2\), Q; + \( x_1 \) CHCl\(_3\), \( \Delta \); + \( x_2 \) CCl\(_4\), \( \Box \). The continuous curves were calculated from Eq. (5).

Table 3—Values of the parameters and standard percentage deviations for (diethylene glycol dibutyl ether + chloroalkanes) systems represented by Eqs. (8-13) and (7-13)

<table>
<thead>
<tr>
<th></th>
<th>Eq. 7</th>
<th>Eq. 8</th>
<th>Eq. 9</th>
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<tbody>
<tr>
<td></td>
<td>( \alpha ) %</td>
<td>( G_{12} )</td>
<td>( \sigma ) %</td>
</tr>
<tr>
<td>Diethylene glycol</td>
<td>28.24</td>
<td>2.41</td>
<td>1.49</td>
</tr>
<tr>
<td>dibutyl ether +</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>31.33</td>
<td>2.54</td>
<td>10.39</td>
</tr>
<tr>
<td>Trichloromethane</td>
<td>16.58</td>
<td>1.13</td>
<td>4.17</td>
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<tr>
<th></th>
<th>Eq. 10</th>
<th>Eq. 11</th>
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<tbody>
<tr>
<td></td>
<td>( H_{12} )</td>
<td>( W_{\text{E}^{\text{RT}}} )</td>
</tr>
<tr>
<td>Diethylene glycol</td>
<td>1.94</td>
<td>1.93</td>
</tr>
<tr>
<td>dibutyl ether +</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>2.52</td>
<td>2.56</td>
</tr>
<tr>
<td>Trichloromethane</td>
<td>2.16</td>
<td>1.16</td>
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</tbody>
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<table>
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<tr>
<th></th>
<th>Eq. 12</th>
<th>Eq. 13</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>( Z_{12} )</td>
<td>( Z_{13} )</td>
</tr>
<tr>
<td>Diethylene glycol</td>
<td>0.61</td>
<td>1.07</td>
</tr>
<tr>
<td>dibutyl ether +</td>
<td></td>
<td></td>
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<tr>
<td>Dichloromethane</td>
<td>0.64</td>
<td>1.20</td>
</tr>
<tr>
<td>Trichloromethane</td>
<td>0.68</td>
<td>0.67</td>
</tr>
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from 16.6 to 31.3 % for Eq. (7) without any adjustable parameter; from 1.2 to 12.6% for single parameter equations (Eqs 8-11); from 1.3 to 2.6 % for the two parameters equation (Eq. 12); and from 0.3 to 0.4% for the three parameters equation (Eq. 13). As can be clearly seen by the results of Eqs (8-11) in Table 3, Eqs (8) and (11) of Grunberg-Nissan and Katti and Chaudhary give nearly identical results. Both Tamura and Kurata \(^5\) (Eq. 9) and Hind et al. \(^3\) (Eq. 10) represent the behaviour of binary mixtures satisfactorily as compared to Grunberg and Nissan \(^1\) (Eq. 8) and Katti
and Chaudhary 34 (Eq. 11). The values of σ are in the range from 1.3 to 2.6% for Eq. 12 with two parameters and from 0.3 to 0.4% for three parameters Eq. 13. Use of the three parameters equation reduces the σ values significantly below that of the two parameters equation. From this study, it can be concluded that the correlating ability significantly improves for these non ideal systems as the number of adjustable parameters is increased.

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References