Densities and Viscosities of 1-Pentanol Binary Mixtures at 293.15 K

Nikos G. Tsierkezos, Maria M. Palaiologou, and Ioanna E. Molinou*

Physical Chemistry Laboratory, Department of Chemistry, University of Athens, Panepistimiopolis, Athens 157 71, Greece

Densities (\(\rho\)) and viscosities (\(\eta\)) for binary mixtures of 1-pentanol with benzene, chlorobenzene, bromobenzene, iodobenzene, nitrobenzene, aniline, toluene, and p-xylene have been measured over the whole composition range at 293.15 K. The excess volumes \(V^E\) and the viscosity deviations \(\Delta\eta\) were calculated, and the results were fitted to a Redlich–Kister type polynomial relation. The corresponding parameters have been derived. The resulting excess functions were interpreted in terms of the interactions between the molecules in the binary mixtures.

**Introduction**

A study of molecular interactions in binary liquid mixtures has been the subject of active investigation in our laboratories in recent years (Palaiologou and Molinou, 1995; Tsierkezos and Molinou, 1998).

Alcohols are interesting polar solvents, self-associated through hydrogen bonding, creating multimers of different degrees (Dewan et al., 1991; Dewan et al., 1992).

Recently, excess volumes and viscosity deviations of binary mixtures of alkanols have been extensively studied (Dewan et al., 1991; Dewan et al., 1992; Aminabhavi et al., 1993; Nikam et al., 1995; Bhardwaj et al., 1996; Garcia and Korosi and Kovats, 1981. Thermodynamic properties of binary mixtures containing substituted benzenes have also been reported (Qin et al., 1992; Yadava et al., 1994; Ramadevi and Prabhakara Rao, 1995; Ramachandran et al., 1995).

1-Pentanol in its pure form is assumed to create monomers and cyclic dimers (Dewan et al., 1992). A mixture of 1-pentanol with another organic compound will lead to specific interactions depending on the proton-accepting ability of the other molecule. This process will determine the volume deviation from ideality.

Regarding values of \(V^E\) of mixtures of lower alkanols with benzene and its substitutes, already measurements for methanol, ethanol, 1-propanol, 1-butanol with nitrobenzene at 298.15 and 303.15 K (Nikam et al., 1995), 1-butanol with benzene at 298.15 and 308.15 K (Yu and Tsai, 1994), and 1-butanol with p-xylene at 308.15 K (Bhardwaj et al., 1996) have been reported.

In this work we report the experimental densities and viscosities for binary mixtures of 1-pentanol with benzene, chlorobenzene, bromobenzene, iodobenzene, nitrobenzene, aniline, toluene, and p-xylene at 293.15 K. From these results the excess volumes and viscosity deviations were derived. The aim of this work is to compare the effect of the various substituents on the benzene molecule on the intermolecular interactions.

No literature data on excess molar volumes and viscosities are available for these mixtures except for benzene + 1-pentanol at 298.15 and 323.15 K (Ortega and Paz-Andrade, 1986) and for the same mixture at 298.15 and 308.15 K (Yu and Tsai, 1994).

**Table 1. Comparison of Experimental Densities \(\rho\) and Refractive Indices \(n_0\) of Pure Liquids with Literature Values at 293.15 K**

<table>
<thead>
<tr>
<th>Liquid</th>
<th>(\rho(\text{exp})) g cm(^{-3})</th>
<th>(\rho(\text{ref})) g cm(^{-3})</th>
<th>(n_0(\text{exp}))</th>
<th>(n_0(\text{ref}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-pentanol</td>
<td>0.814 68</td>
<td>0.814 80</td>
<td>1.4108</td>
<td>1.4100</td>
</tr>
<tr>
<td>benzene</td>
<td>0.878 91</td>
<td>0.879 32</td>
<td>1.5015</td>
<td>1.50113</td>
</tr>
<tr>
<td>chlorobenzene</td>
<td>1.106 46</td>
<td>1.105 86</td>
<td>1.5247</td>
<td>1.5250</td>
</tr>
<tr>
<td>bromobenzene</td>
<td>1.494 66</td>
<td>1.495 04</td>
<td>1.5597</td>
<td>1.5600</td>
</tr>
<tr>
<td>iodobenzene</td>
<td>1.825 92</td>
<td>1.831 60</td>
<td>1.6196</td>
<td>1.6201</td>
</tr>
<tr>
<td>nitrobenzene</td>
<td>1.203 29</td>
<td>1.202 60</td>
<td>1.5527</td>
<td>1.5525</td>
</tr>
<tr>
<td>aniline</td>
<td>1.021 66</td>
<td>1.020 58</td>
<td>1.5860</td>
<td>1.5865</td>
</tr>
<tr>
<td>toluene</td>
<td>0.866 89</td>
<td>0.867 20</td>
<td>1.4971</td>
<td>1.4970</td>
</tr>
<tr>
<td>p-xylene</td>
<td>0.863 14</td>
<td>0.861 27</td>
<td>1.4962</td>
<td>1.4958</td>
</tr>
</tbody>
</table>

* Corresponding author. E-mail: imolinou@cc.uoa.gr.

**Experimental Section**

**Materials.** The reagents toluene (Merck p.a. > 99.5%), aniline (Merck p.a. > 99.8%), benzene (Merck p.a. > 99.5%), chlorobenzene (Fluka p.a. > 99.0%), bromobenzene (Fluka p.a. > 99.0%), iodobenzene (Fluka p.a. > 99.5%), 1-pentanol (Fluka p.a. > 99.5%), nitrobenzene (Fluka p.a. > 99.5%), and p-xylene (Merck > 99.0%) were used without purification. The purity of the liquids was assessed by comparing the densities and refractive indices with the literature values (Table 1). The agreement was satisfactory.

The binary mixtures were prepared by mass (Mettler A210P, ±0.01 mg). The mole fractions were known to ±0.0001 in all cases.
The estimated uncertainty of the measured densities is ±0.00001 g·cm⁻³. The DMA cell was calibrated with dry air and doubly distilled water at atmospheric pressure. The sample size was 0.7 cm³, and the sample thermostat was controlled to ±0.01 K.

The flow times of the mixtures and the pure liquids were measured with an automated Schott Geräte AVS 310 Unit, equipped with an Ubbelohde capillary viscometer. The viscometer was calibrated with doubly distilled water. The accuracy in the flow times was ±0.01 s. The viscometer was placed in a thermostat (model Schott CT 050/2) maintained constant within ±0.03 K. The absolute viscosities \( \eta \) were calculated from the kinematic viscosities \( \nu \) using the density values \( \rho \) for each mixture (\( \eta = \nu \rho \)). The accuracy of the kinematic viscosities (±0.001 mm²·s⁻¹) and the densities (±0.00001 g·cm⁻³) gives the maximum uncertainty ±0.001 mPa·s in the absolute viscosities.

### Results and Discussion

The experimental values of density and viscosity for all mixtures at different compositions and at 293.15 K are listed in Table 2.

The values of excess molar volumes \( V^E \) and viscosity deviations \( \Delta \eta \) were calculated from the experimental data according to the following equations:

\[
V^E = V_m - \sum_{i=1}^{2} V_i x_i
\]

(1)

\[
\Delta \eta = \eta_m - \sum_{i=1}^{2} \eta_i x_i
\]

(2)

where \( x_i, V_i, \) and \( \eta_i \) represent the mole fraction, the molar volume, and the viscosity of the \( i \)th pure component of the mixture. \( V_m \) and \( \eta_m \) are the molar volume and the viscosity of the mixture, respectively. The molar volume \( V_m \) of the mixture was calculated from the following equation:

\[
V_m = \sum_{i=1}^{2} x_i M_i / \rho_m
\]

(3)

where \( \rho_m \) is the mixture density and \( M_i \) is the molecular weight of component \( i \) in the mixture.

The experimental values of \( V^E \) and \( \Delta \eta \) are fitted to the Redlich–Kister equation:

\[
Y = x_1 x_2 \sum_{k=0}^{n} A_k (2x_1 - 1)^k
\]

(4)

where \( Y \) represents the excess volume or the viscosity deviations and \( A_k \) represents the parameters.

The number of parameters \( A_k \) used was obtained from the calculated and experimental values according to the equation

\[
\sigma = \left[ \sum (Y_{\text{exp}} - Y_{\text{calc}})^2 / (n - p) \right]^{1/2}
\]

(5)

where \( n \) and \( p \) are the number of experimental points and parameters, respectively, and \( \sigma \) is the standard deviation. The values of \( A_k \) and \( \sigma \) are presented in Table 3.

In Figures 1 and 2 the \( V^E \) values are positive for a 1-pentanol + benzene mixture, change to sigmoidal for aryl halides, toluene, and p-xylene, and are negative for nitrobenzene and aniline.

The behavior of the 1-pentanol + benzene mixture may be attributed to the disruption of the hydrogen-bonded alcohol by the nonpolar benzene (Yu and Tsai, 1994).
The sigmoidal curves show that the negative values are at the 1-pentanol-rich region. The breaking up of the self-associated 1-pentanol, which leads to a volume increase, and the specific interactions, such as hydrogen bond formation between the 1-pentanol and the substituted benzene (Crabtree, 1998; Rastogi et al., 1967; Garcia et al., 1997), which lead to a volume reduction, seem to contribute to the sigmoidal curves.

The strong negative values for the mixtures 1-pentanol + aniline can be interpreted as a consequence of the strong attractions appearing between the hydrogen of the OH group and the lone pair of electrons in the NH₂ group. Furthermore, the high dipole moment of nitrobenzene (3.96 D at 20 °C) (Daniels and Alberty, 1975) favors dipole–dipole interactions, leading also to a volume reduction to

Table 3. Parameters and Standard Deviations of Excess Functions of 1-Pentanol Binary Mixtures

<table>
<thead>
<tr>
<th>function</th>
<th>A₀</th>
<th>A₁</th>
<th>A₂</th>
<th>A₃</th>
<th>σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vₚ/cm³ mol⁻¹</td>
<td>1-Pentanol (1) + Benzene (2)</td>
<td>1.0857</td>
<td>−0.6211</td>
<td>0.1417</td>
<td>0.0065</td>
</tr>
<tr>
<td>Δη/mPa s</td>
<td>−4.2109</td>
<td>−1.4039</td>
<td>−0.0845</td>
<td>0.4951</td>
<td>0.0088</td>
</tr>
<tr>
<td>Vₚ/cm³ mol⁻¹</td>
<td>1-Pentanol (1) + Chlorobenzene (2)</td>
<td>−0.3516</td>
<td>−0.6410</td>
<td>0.0518</td>
<td>−0.2230</td>
</tr>
<tr>
<td>Δη/mPa s</td>
<td>−3.7985</td>
<td>−1.2033</td>
<td>0.0536</td>
<td>0.5878</td>
<td>0.0078</td>
</tr>
<tr>
<td>Vₚ/cm³ mol⁻¹</td>
<td>1-Pentanol (1) + Bromobenzene (2)</td>
<td>−0.3830</td>
<td>−0.5602</td>
<td>0.0069</td>
<td>−0.2360</td>
</tr>
<tr>
<td>Δη/mPa s</td>
<td>−3.3715</td>
<td>−0.9160</td>
<td>0.0445</td>
<td>0.8927</td>
<td>0.0064</td>
</tr>
<tr>
<td>Vₚ/cm³ mol⁻¹</td>
<td>1-Pentanol (1) + Iodobenzene (2)</td>
<td>−0.2490</td>
<td>−0.3792</td>
<td>−0.1517</td>
<td>−0.6929</td>
</tr>
<tr>
<td>Δη/mPa s</td>
<td>−3.2162</td>
<td>−0.2121</td>
<td>−0.2819</td>
<td>0.0082</td>
<td></td>
</tr>
<tr>
<td>Vₚ/cm³ mol⁻¹</td>
<td>1-Pentanol (1) + Nitrobenzene (2)</td>
<td>−0.5317</td>
<td>−0.4622</td>
<td>−0.9069</td>
<td>−0.5766</td>
</tr>
<tr>
<td>Δη/mPa s</td>
<td>−3.5097</td>
<td>−1.0677</td>
<td>−1.5524</td>
<td>0.4790</td>
<td>0.0053</td>
</tr>
<tr>
<td>Vₚ/cm³ mol⁻¹</td>
<td>1-Pentanol (1) + Aniline (2)</td>
<td>−1.0625</td>
<td>−0.1678</td>
<td>−0.2529</td>
<td>−0.3953</td>
</tr>
<tr>
<td>Δη/mPa s</td>
<td>−4.6146</td>
<td>0.4033</td>
<td>−2.1165</td>
<td>0.0084</td>
<td></td>
</tr>
<tr>
<td>Vₚ/cm³ mol⁻¹</td>
<td>1-Pentanol (1) + Toluene (2)</td>
<td>0.1905</td>
<td>−0.5031</td>
<td>0.0740</td>
<td>−0.1559</td>
</tr>
<tr>
<td>Δη/mPa s</td>
<td>−4.4324</td>
<td>−1.7122</td>
<td>−0.1572</td>
<td>0.3270</td>
<td>0.0040</td>
</tr>
<tr>
<td>Vₚ/cm³ mol⁻¹</td>
<td>1-Pentanol (1) + p-Xylene (2)</td>
<td>−0.0065</td>
<td>−0.4934</td>
<td>−0.0339</td>
<td>−0.0589</td>
</tr>
<tr>
<td>Δη/mPa s</td>
<td>−4.5335</td>
<td>−2.0052</td>
<td>−0.3895</td>
<td>0.2037</td>
<td>0.0054</td>
</tr>
</tbody>
</table>
the 1-pentanol + nitrobenzene mixture (Nikam et al., 1995).

In Figure 3 we compare our \( V^E \) values of the binary 1-pentanol + benzene mixture with the reference values. The agreement is quite satisfactory.

The results for \( \Delta V \) are represented graphically in Figures 4 and 5. The \( \Delta V \) values are negative for all systems investigated. For the mixtures 1-pentanol + benzene, + chlorobenzene, + bromobenzene, and + iodobenzene (Figure 4), the algebraic values of \( \Delta V \) fall in the order iodobenzene > bromobenzene > chlorobenzene > benzene, reflecting an easier flow of the mixture at the direction of decreasing molecular weight of the aryl halide.

**Literature Cited**


Fornefeld-Schwarz, U. M.; Svedja, P. Refractive Indices and Relative Permittivities of Liquid Mixtures of \( \gamma \)-Butyro lactone, \( \gamma \)-Valerolactone, \( \gamma \)-Valerolactone, \( \alpha \)-Caprolactone + Benzene, + Toluene, or + Ethylbenzene at 293.15 K and 313.15 K and Atmospheric Pressure. J. Chem. Eng. Data 1999, 44, 597–604.


TRC Databases for Chemistry and Engineering: Thermodynamics Research Center, Texas A & M University System: College Station, TX, 1991–98.


Received for review July 27, 1999. Accepted November 15, 1999.