Vapor pressure, density, viscosity and refractive index of dimethyl sulfoxide + 1,4-dimethylbenzene system

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Abstract: This paper reports the experimental results of isothermal vapor–liquid equilibrium data between 303.15 and 333.15 K, and densities, viscosities, refractive indices from 298.15 to 323.15 K of the dimethyl sulfoxide + 1,4-dimethylbenzene system over the entire range of mixture composition. The obtained PTX data were correlated by the Wilson and NRTL models and estimated by the UNIFAC model. The excess Gibbs energy and activity coefficients were calculated and compared with others excess properties. Excess molar volumes, viscosity deviations and deviations in refractivity were calculated from the experimental data; all the computed quantities were fitted to the Redlich–Kister equation. The resulting excess functions were interpreted in terms of structure and interactions.

Keywords: dimethyl sulfoxide; 1,4-dimethylbenzene; VLE data; density; viscosity; excess properties.

INTRODUCTION

Continuing our work on the thermodynamics of non-electrolyte systems, the present paper is a part of a study of binary systems containing dimethyl sulfoxide (DMSO) and aromatic hydrocarbons, interesting as mixed solvents.1 Dimethyl sulfoxide is a versatile non-aqueous, aprotic, highly polar self-associated solvent used extensively in kinetic studies, electrochemistry and as a solvent for polymers. Binary mixtures of DMSO with aromatic solvents are interesting in studies of polymer miscibility, polymer phase diagrams and preferential interactions in mixed solvents.2

This paper reports experimental isothermal vapor liquid equilibrium (VLE) data at temperatures 303.15, 313.15, 323.15 and 333.15 K and experimental data of density, viscosity and refractive index at temperatures 298.15, 303.15, 313.15 and 323.15 K for the dimethyl sulfoxide + 1,4-dimethylbenzene system.

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The VLE data were correlated by means of the Wilson\textsuperscript{3} and NRTL\textsuperscript{4} models; this work also served to test the predictive capacity of the group contribution methods: original UNIFAC\textsuperscript{5} and UNIFAC–Dortmund.\textsuperscript{6,7} Excess molar volumes, viscosity deviations and deviations in refractivity were calculated from the experimental data; all the computed quantities were fitted to the Redlich–Kister equation.

A survey of the literature\textsuperscript{8} revealed only one source of VLE data for this binary system, in which the data are presented only as diagrams.\textsuperscript{9} A few studies which considered the volumetric properties have been reported;\textsuperscript{10–12} no literature data on viscosities and refractive indices are available for this system.

**EXPERIMENTAL**

**Materials**

The employed chemicals were purified by distillation. Dimethyl sulfoxide was distilled under vacuum at 0.8–0.9 kPa and 338.65 K. The analytical-reagent-grade 1,4-dimethylbenzene from Fluka (p.a.) was used without further purification. The pure substances were kept in airtight stoppered glass bottles to avoid air contact. The purity was checked by refractive index, density and gas chromatography. It was better than 99.5 mass %. The physical properties were checked by repeated measurements over an interval of 2–3 days, during which time no changes were observed. The experimental values of density, refractive index and viscosity of the pure components are presented in Table I and compared with literature values.

**TABLE I.** Experimental and literature values for the density ($\rho$), refractive index ($n_D$) and viscosity ($\eta$) of the pure components

<table>
<thead>
<tr>
<th>$T$ / K</th>
<th>$\rho \times 10^3$ / kg·m\textsuperscript{-3}</th>
<th>$n_D$</th>
<th>$\eta$ / mPa·s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl sulfoxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>293.15</td>
<td>1.10050\textsuperscript{13}</td>
<td>1.10073</td>
<td>1.4770\textsuperscript{15}</td>
</tr>
<tr>
<td>298.15</td>
<td>1.09571\textsuperscript{12}</td>
<td>1.09574</td>
<td>1.4770\textsuperscript{15}</td>
</tr>
<tr>
<td>303.15</td>
<td>1.09000\textsuperscript{12}</td>
<td>1.09074</td>
<td>1.4752\textsuperscript{14}</td>
</tr>
<tr>
<td>313.15</td>
<td>1.08182\textsuperscript{12}</td>
<td>1.08075</td>
<td>1.4700\textsuperscript{14}</td>
</tr>
</tbody>
</table>

1,4-Dimethylbenzene

<table>
<thead>
<tr>
<th>$T$ / K</th>
<th>$\rho \times 10^3$ / kg·m\textsuperscript{-3}</th>
<th>$n_D$</th>
<th>$\eta$ / mPa·s</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>0.8611\textsuperscript{19}</td>
<td>0.86144</td>
<td>1.49320\textsuperscript{10}</td>
</tr>
<tr>
<td>298.15</td>
<td>0.8568\textsuperscript{12}</td>
<td>0.85712</td>
<td>1.49286\textsuperscript{20}</td>
</tr>
</tbody>
</table>

**Procedure**

The binary mixtures were prepared by mixing the appropriate volumes of liquids in airtight stoppered glass bottles and weighed using an HR-120 (A & D Japan) electronic balance with a precision of 0.0001 g. The experimental uncertainty in the mole fractions was estimated to be less than ±0.0002.
The total vapor pressure of the binary mixtures was measured at temperatures between 303.15 and 333.15 K by a static non analytic (synthetic) method, with a glass isotensioscope of the Smith and Menzies type, which allows the measurements of VLE at subatmospheric pressures at temperatures up to 423.15 K. Experimental apparatus used in this work was the same as that used in a previous study. A schematic diagram of the apparatus is shown in Fig. 1. The apparatus consists of an equilibrium cell placed in a constant-temperature water bath. The experimental procedure was typical for static VLE measurements: a sample of known composition with a volume of about 4–5 cm³ was introduced into the equilibrium cell at the beginning of each experiment, degassed by the freeze-thaw method under vacuum and then the temperature of the entire system was maintained constant by controlling the temperature of the water bath. After the desired temperature was attained, the total pressure was measured for the liquid mixture in the equilibrium cell. The temperature in the water bath was controlled by a U-10 type thermostat and measured with an Hg thermometer with an estimated accuracy of 0.05 K. The vapor pressures were measured by means of an Hg manometer and a cathetometer, with accuracy to within 0.026 kPa. As the vapor phase volume of the cell was relatively small, calculation showed that the error in composition due to vaporization is within this limit.

The densities, ρ, of the pure solvents and the mixtures were measured with an Anton Paar DMA 4500 densitometer with a precision of ±0.00005 g cm⁻³, between 298.15 and 323.15 K. The DMA cell was calibrated with dry air and ultra pure water at atmospheric pressure. The sample size was 0.7 cm³ and the sample thermostat was controlled to ±0.01 K. Triplicate measurements of the density were performed for all the mixtures and pure components. The accuracy in the determination of the density is believed to be less than ±0.2 kg m⁻³ and ±10⁻⁸ m³·mol⁻¹ for the calculation of $\tau^E$.

The kinematic viscosity, ν, of the pure components and their mixtures were determined at the same temperatures as were employed for the density measurements using an Ubbelohde capillary viscometer having a capacity of about 15 ml, a length of about 90 mm and 0.5 mm internal diameter. The viscometer was calibrated using doubly distilled water. At least four time flow measurements were performed for each composition and temperature, and the results were averaged. The viscometer was kept vertically in a transparent-walled bath with a thermal stability of ±0.05 K for about 30 min to attain thermal equilibrium. The uncertainty of
the flow time measurement was ±0.1 s. The corresponding uncertainty in the kinematic viscosity is ±0.001 $10^{-6}$ m$^2$ s$^{-1}$.

Refractive indices values for the D-line, $n_D$, were measured with a thermostated Abbe refractometer with a precision of ±0.0001. All measurements were performed in a thermostat maintained at ±0.05 K.

RESULTS AND DISCUSSION

The measurements of total pressure were carried out at various compositions in the investigated temperature range. For each binary mixture, the dependencies between the experimental pressure and temperature were established. The functions $p = f(T)$ obtained by polynomial regression were used to calculate the VLE data at 303.15, 313.15, 323.15 and 333.15 K. The smoothed data resulting from the experimental measurements are reported in Table II. The temperature dependence of the vapor pressures of the pure component was calculated using the Antoine equation.24, 25

<table>
<thead>
<tr>
<th>$T$ / K</th>
<th>$x_1$</th>
<th>303.15</th>
<th>313.15</th>
<th>323.15</th>
<th>333.15</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>11.63</td>
<td>19.85</td>
<td>32.53</td>
<td>51.44</td>
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</tr>
<tr>
<td>0.1235</td>
<td>12.51</td>
<td>18.74</td>
<td>32.50</td>
<td>54.10</td>
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<tr>
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<td>18.06</td>
<td>32.76</td>
<td>54.00</td>
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<td>8.95</td>
<td>16.40</td>
<td>30.00</td>
<td>52.01</td>
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<td>0.4059</td>
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<td>15.73</td>
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<td>14.31</td>
<td>27.01</td>
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</tr>
<tr>
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<td>8.17</td>
<td>12.84</td>
<td>22.88</td>
<td>38.31</td>
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<tr>
<td>0.9078</td>
<td>5.54</td>
<td>10.48</td>
<td>17.60</td>
<td>26.90</td>
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</tr>
<tr>
<td>0.9554</td>
<td>4.83</td>
<td>6.41</td>
<td>11.01</td>
<td>18.63</td>
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</tr>
<tr>
<td>1</td>
<td>0.85</td>
<td>1.66</td>
<td>3.07</td>
<td>5.46</td>
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</tr>
</tbody>
</table>

Various models are used for the correlation and prediction of binary VLE data: the Equations based on the local composition concept (Wilson and NRTL) and the group contribution methods, UNIFAC.

The results of the correlation with the Wilson and NRTL models are presented in Table III, which includes the values of the model parameters and the statistical parameters: average percentage deviation in pressure, $\Delta p$, and standard deviation, $\sigma$.

Prediction of the VLE data for the binary system at the investigated temperatures was performed using the original UNIFAC method and its modification, UNIFAC–Dortmund. The group interaction parameters were those published by Reid,26 Hansen27 and Gmehling.6,7 The results of the predictions are also presented in Table III.
TABLE III. Results of the correlation and prediction with the Wilson, NRTL and UNIFAC models for the dimethyl sulfoxide (1) + 1,4-dimethylbenzene (2) system

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters (J mol⁻¹)</th>
<th>Statistical parameters</th>
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<tr>
<td></td>
<td></td>
<td>σ (mm Hg)</td>
<td>Δp (%)</td>
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<tr>
<td>303.15 K</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Wilson</td>
<td>Δχ₁₂ = 4143.8</td>
<td>0.86</td>
<td>7.14</td>
<td></td>
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<tr>
<td></td>
<td>Δχ₂₁ = 2412.5</td>
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<tr>
<td>NRTL (α = 0.3)</td>
<td>Δg₁₂ = 4067.7</td>
<td>0.91</td>
<td>7.54</td>
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<td></td>
<td>Δg₂₁ = 1442.6</td>
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<tr>
<td>Original UNIFAC</td>
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<td></td>
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<tr>
<td>UNIFAC–Dortmund</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>313.15 K</td>
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<td></td>
</tr>
<tr>
<td>Wilson</td>
<td>Δχ₁₂ = 3764.3</td>
<td>0.41</td>
<td>2.64</td>
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<tr>
<td></td>
<td>Δχ₂₁ = 346.4</td>
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<tr>
<td>NRTL (α = 0.3)</td>
<td>Δg₁₂ = 4444.2</td>
<td>0.37</td>
<td>2.10</td>
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<tr>
<td></td>
<td>Δg₂₁ = 969.4</td>
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<tr>
<td>Original UNIFAC</td>
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<tr>
<td>UNIFAC–Dortmund</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>323.15 K</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wilson</td>
<td>Δχ₁₂ = 6261.8</td>
<td>0.86</td>
<td>2.27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Δχ₂₁ = 1163.9</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>NRTL (α = 0.3)</td>
<td>Δg₁₂ = 2620.0</td>
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<tr>
<td></td>
<td>Δg₂₁ = 3451.0</td>
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<tr>
<td>Original UNIFAC</td>
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<td></td>
</tr>
<tr>
<td>UNIFAC–Dortmund</td>
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</tr>
<tr>
<td>333.15 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wilson</td>
<td>Δχ₁₂ = 9770.9</td>
<td>1.07</td>
<td>1.91</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Δχ₂₁ = 455.2</td>
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<tr>
<td>NRTL (α=0.3)</td>
<td>Δg₁₂ = 1649.8</td>
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<td>3.85</td>
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<tr>
<td></td>
<td>Δg₂₁ = 5777.3</td>
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<tr>
<td>Original UNIFAC</td>
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<td></td>
</tr>
<tr>
<td>UNIFAC–Dortmund</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| aStandard deviation σ = \(\sum_i\{(p_{calc}(i) - p_{exp}(i))^2 / (N - M)\}^{0.5}\) (N: number of data points and M: number of estimated parameters); bAverage percentage deviation in pressure Δp = (100 / N)\(\sum_i\{p_{calc}(i) - p_{exp}(i)\} / p_{exp}(i)\)

The Wilson and NRTL method give similar and good representation of the experimental data (except at 303.15 K); the values of σ and Δp characterize the data as satisfactory. It can be observed that the description of this system by the original UNIFAC method shows good agreement with the experimental data, as do the Wilson and NRTL models; the modified UNIFAC method gave less satisfactory results, especially at higher temperatures.

The experimental and calculated (with the Wilson model) total pressures vs. the liquid and vapor compositions for 303.15, 313.15, 323.15 and 333.15 K are presented in Fig. 2. The activity coefficients were calculated using the Wilson equation for the binary systems. The dependence of the activity coefficient on
composition at 313.15 K are presented in Fig. 3, the limiting values at infinite dilution of these coefficients also being given. The variation of the excess Gibbs energy of the system was also computed and represented, which showed positive deviations from ideality. Comparison of maximum obtained value of $G^E$ at 313.15 K with literature is satisfactory.\textsuperscript{9}

![Fig. 2. Experimental vapor pressures of the dimethyl sulfoxide (1) + 1,4-dimethylbenzene (2) system at 303.15 K (○); 313.15 K (△); 323.15 K (○); 333.15 K (×); correlation with the Wilson model (—).](image)

![Fig. 3. Activity coefficients and excess Gibbs energy for the dimethyl sulfoxide (1) + 1,4-dimethylbenzene (2) system calculated with the Wilson model at 313.15 K.](image)

The densities, viscosities and refractive indices were measured in the temperature range from 298.15 to 323.15 K and the measured values are listed in Table IV. The experimental densities correspond well with existing literature data.\textsuperscript{10–12} The values of the excess molar volume, $V^E$, viscosity deviation, $\Delta \nu$, and deviation in molar refractivity, $\Delta R$, were calculated from the experimental data according to the following equations:

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

\[ \Delta \nu = \nu_m - \sum_{i=1}^{2} \nu_i x_i \]  \hspace{1cm} (2)

\[ \Delta R = R_m - \sum_{i=1}^{2} R_i \varphi_i \]  \hspace{1cm} (3)

where $x_i$ and $\varphi_i$ represent the mole fraction and volume fraction of the pure component $i$, respectively; $V_m$, $\nu_m$, and $R_m$ the properties of the mixtures and $V_i$, $\nu_i$, and $R_i$, the properties of the pure components. The values of $\Delta R$ were calculated from the Lorentz–Lorenz equation.\textsuperscript{28} The experimental excess molar volumes and deviations in viscosity are reported in Table IV.
TABLE IV. Experimental density, kinematic viscosity, refractive index, excess molar volume and viscosity deviation for the dimethyl sulfoxide (1) + 1,4-dimethylbenzene (2) system from 298.15 to 323.15 K

<table>
<thead>
<tr>
<th>x_1</th>
<th>( \rho \times 10^3 ) kg m(^{-3})</th>
<th>( \nu \times 10^6 ) m(^2) s(^{-1})</th>
<th>( \Delta \nu \times 10^6 ) m(^2) s(^{-1})</th>
<th>( n_D )</th>
<th>x_1</th>
<th>( \rho \times 10^3 ) kg m(^{-3})</th>
<th>( \nu \times 10^6 ) m(^2) s(^{-1})</th>
<th>( \Delta \nu \times 10^6 ) m(^2) s(^{-1})</th>
<th>( n_D )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>298.15 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>303.15 K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0000</td>
<td>0.85712</td>
<td>0.000</td>
<td>0.0000</td>
<td>0.733</td>
<td>0.000</td>
<td>1.4930</td>
<td>0.6077</td>
<td>0.97178</td>
<td>-0.206</td>
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<td>-0.086</td>
<td>0.1056</td>
<td>0.788</td>
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</tr>
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</tr>
<tr>
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<tr>
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<td>0.0000</td>
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<td>0.95786</td>
<td>-0.223</td>
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<td>0.85928</td>
<td>-0.079</td>
<td>0.1056</td>
<td>0.672</td>
<td>-0.042</td>
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<td>0.7048</td>
<td>0.98319</td>
<td>-0.196</td>
</tr>
<tr>
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<td>0.2988</td>
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<td>-0.060</td>
<td>-</td>
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<td>0.2988</td>
<td>0.690</td>
<td>-0.082</td>
<td>-</td>
<td>0.9002</td>
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<td>-0.108</td>
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</table>
The experimental values of $V^E$, $\Delta \nu$ and $\Delta R$ were fitted to Redlich–Kister type polynomials:

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

where $Y$ is $V^E$, $\Delta \nu$ or $\Delta R$ and $A_k$ represents the parameters. A nonlinear least-squares method was used to estimate the adjustable parameters $A_k$. The values of $A_k$ and standard deviation $\sigma$ are given in Table V.

Table V. The adjustable parameters and standard deviations of the excess functions of the dimethyl sulfoxide (1) + 1,4-dimethylbenzene (2) system

<table>
<thead>
<tr>
<th>Function</th>
<th>$A_0$</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$A_3$</th>
<th>$\sigma_a^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V^E \times 10^6 / \text{m}^3 \text{ mol}^{-1}$</td>
<td>$-0.8664$</td>
<td>$-0.0306$</td>
<td>$-0.1530$</td>
<td>$0.1023$</td>
<td>$0.0009$</td>
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<tr>
<td>$\Delta \nu \times 10^6 / \text{m}^2 \text{ s}^{-1}$</td>
<td>$-0.7866$</td>
<td>$-0.1422$</td>
<td>$-0.0365$</td>
<td>$0.0004$</td>
<td></td>
</tr>
<tr>
<td>$\Delta R \times 10^6 / \text{m}^3 \text{ mol}^{-1}$</td>
<td>$-8.6332$</td>
<td>$2.0491$</td>
<td>$-0.5638$</td>
<td>$0.1739$</td>
<td>$0.0022$</td>
</tr>
<tr>
<td>$V^E \times 10^6 / \text{m}^3 \text{ mol}^{-1}$</td>
<td>$-0.8656$</td>
<td>$-0.0465$</td>
<td>$-0.1566$</td>
<td>$0.1576$</td>
<td>$0.0003$</td>
</tr>
<tr>
<td>$\Delta \nu \times 10^6 / \text{m}^2 \text{ s}^{-1}$</td>
<td>$-0.6709$</td>
<td>$-0.1593$</td>
<td>$-0.0216$</td>
<td>$0.0002$</td>
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</tr>
<tr>
<td>$\Delta R \times 10^6 / \text{m}^3 \text{ mol}^{-1}$</td>
<td>$-8.6048$</td>
<td>$2.2879$</td>
<td>$-0.7394$</td>
<td>$0.0058$</td>
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<tr>
<td>$V^E \times 10^6 / \text{m}^3 \text{ mol}^{-1}$</td>
<td>$-0.9344$</td>
<td>$0.0234$</td>
<td>$0.0460$</td>
<td>$0.1186$</td>
<td>$0.0014$</td>
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<td>$\Delta \nu \times 10^6 / \text{m}^2 \text{ s}^{-1}$</td>
<td>$-0.5201$</td>
<td>$-0.1044$</td>
<td>$-0.0190$</td>
<td>$0.0002$</td>
<td></td>
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<tr>
<td>$\Delta R \times 10^6 / \text{m}^3 \text{ mol}^{-1}$</td>
<td>$-8.5246$</td>
<td>$2.1822$</td>
<td>$-0.8037$</td>
<td>$0.5005$</td>
<td>$0.0041$</td>
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<tr>
<td>$V^E \times 10^6 / \text{m}^3 \text{ mol}^{-1}$</td>
<td>$-0.9598$</td>
<td>$-0.0287$</td>
<td>$-0.2444$</td>
<td>$0.1199$</td>
<td>$0.0010$</td>
</tr>
<tr>
<td>$\Delta \nu \times 10^6 / \text{m}^2 \text{ s}^{-1}$</td>
<td>$-0.4168$</td>
<td>$-0.0705$</td>
<td>$-0.0145$</td>
<td>$0.0001$</td>
<td></td>
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</table>

$^a$Standard deviation $\sigma = \sum (Y_{\text{calc}}(i) - Y_{\text{exp}}(i))^2 / (N - M)^{1/2}$ (N: number of data points and M: number of estimated parameters)

As can be seen from Figs. 4a, 4b and 4c, the main features of the system are that the excess molar volumes, deviations in viscosity and deviations in molar refractivity are all negative.

The excess volumes are moderately negative over the entire composition range and become slightly more negative as the temperature of the mixtures increases from 303.15 to 323.15 K. The present $V^E$ values at 303.15 K compare well with those reported by Wang et al.11 obtained using the same experimental method (vibrating-tube densitometer), as can be seen in Fig. 5.

The dependence of $V^E$ on both composition and temperature for the present mixture may be explained as a balance between positive contributions (the breaking up of the associates or molecular order present in the pure liquids and dispersive interactions between unlike molecules) and negative contributions (inter-
molecular interactions and geometrical fitting between the components). In the present study, dimethyl sulfoxide is an aprotic, highly polar self-associated solvent, having a dipole moment $\mu = 3.96$ D;\textsuperscript{30} 1,4–dimethylbenzene is a non-polar, stable substance with a large quadrupole moment,\textsuperscript{31} which causes molecular order in the pure state. On mixing, the molecular order in the aromatic hydrocarbon will decrease because of the DMSO molecules, whereas the molecular associations in pure DMSO will be disrupted by 1,4–dimethylbenzene. Their binary mixtures are characterized by electron donor–acceptor type interactions in which the aromatic hydrocarbon behaves as an electron donor.\textsuperscript{32} The positive heats of mixing\textsuperscript{9,10} for this system suggests the dominance of molecular dissociation over molecular association. In this case, the observed negative $V_E$ values may be explained by geometrical fitting of the molecules of different molecular sizes into each others structure (at 298.15 K, the molar volumes of the components are: 71.30×10\textsuperscript{−6} for DMSO and 123.87×10\textsuperscript{−6} m\textsuperscript{3} mol\textsuperscript{−1} for 1,4-dimethylbenzene).

Fig. 4. Excess molar volumes (a), viscosity deviations (b) and deviations in molar refractivity (c) for the dimethyl sulfoxide (1) + 1,4-dimethylbenzene (2) system at 298.15 (○), 303.15 (□), 313.15 (△) and 323.15 K (○); correlation with the Redlich–Kister equation (—).
The $\Delta \nu$ values are moderately negative over the whole composition range, rising with temperature. The geometrical fitting of the unlike molecules (structural effect) explains, also, the obtained negative $\Delta \nu$ values. Figs. 4a and 4b clearly indicate that $V^E$ and $\Delta \nu$ do not obey the general rule according to which they should have opposite signs, specific for systems where intermolecular interactions predominate. Therefore, the geometrical factor is more important for this system.

![Graph showing $V^E$ vs. $x_1$](image)

Fig. 5. Comparison of the excess molar volumes for the dimethyl sulfoxide (1) + 1,4-dimethylbenzene (2) system at 303.15 K: our data, (○); Ref. 11, (×); correlation with the Redlich–Kister equation, (—).

Moreover, the DMSO + 1,4-dimethylbenzene system shows positive deviations from the Raoult law, characteristic for systems without strong interactions between unlike molecules, suggesting that the structural effect is predominant in this system. Similar cases are presented in the literature, i.e., negative values of both $V^E$ and $\Delta \eta$ due to structural effects and a positive deviation from the Raoult law, correlated with negative viscosity deviation in systems without strong specific interactions.

In the present system, $V^E$ becomes slightly more negative as the temperature of the mixtures increases from 303.15 to 323.15 K. A similar, but more pronounced, trend of $V^E$ was obtained by Ali et al., an opposite trend being observed by Wang et al. As a rule, the excess volumes become more positive as the temperatures increases, generally true for systems where the interactional factor is predominant. The opposite behavior, already observed in the literature for different systems, could be attributed to the predominance of structural effects. It is felt that this last behavior is more reliable for the DMSO + 1,4-dimethylbenzene system, where structural effects predominate, as has been proved by this comprehensive study.

The $\Delta R$ values are negative for the whole composition range for all mixtures. The values are independent of temperature, according to theory, the molar refractivity depending only on the wavelength of light used for the measurements.
The results for the excess thermodynamic functions are in agreement with the result of experimental VLE data in this work.

CONCLUSIONS

Experimental data concerning the isothermal vapor–liquid equilibriums in the binary 1,4-dimethylbenzene + DMSO system have been presented. Eight different mixtures containing 1,4-dimethylbenzene + DMSO were analyzed. Good agreement between the experimental and calculated values of the pressure was observed for the Wilson and NRTL correlative methods and for the original UNIFAC predictive method.

Experimental data for the densities, kinematic viscosities and refractive indices for the binary system DMSO + 1,4–dimethylbenzene are reported. Excess functions were calculated and fitted to the Redlich–Kister equation. All the excess functions are negative over the whole composition range. The trends in the dependence on composition of the excess properties are in agreement with the result of the experimental VLE data and indicate that the contribution from structural effects is predominant over interactional contributions in this system.

SYMBOLS

- $A_i, B_i, C_i$ – Parameters of the Antoine equation
- $A_k$ – Redlich–Kister parameters
- $G^E$ – Excess Gibbs energy
- $g_{ij}$ – Parameters of the NRTL equation
- $M$ – Number of model parameters
- $N$ – Number of experimental points
- $n_D$ – Refractive index
- $\Delta p$ – Average percentage deviation in pressure
- $P_{\text{exp}}$ – Experimental total pressure
- $P_{\text{calc}}$ – Computed total pressure
- $P_i^0$ – Vapor pressure of the $i$–th pure component
- $\Delta R$ – Deviation in molar refractivity
- $R_m$ – Molar refractivity of mixture
- $R_i$ – Molar refractivity of the $i$–th pure component
- $T$ – Absolute temperature
- $V^E$ – Excess molar volume
- $V_m$ – Molar volume of mixture
- $V_i$ – Molar volume of the $i$–th pure component
- $x_i$ – Liquid-phase mole fractions

Greek letters

- $\gamma_k$ – Activity coefficients
- $\lambda_{ij}$ – Parameters of Wilson equation
- $\mu$ – Dipole moment
- $\eta, \nu$ – Dynamic and kinematic viscosity, respectively
- $\Delta \nu$ – Viscosity deviation
- $\nu_m$ – Kinematic viscosity of mixture
ИЗВОД
НАПОН ПАРЕ, ГУСТИНА И ИНДЕКС РЕФРАКЦИЈЕ СИСТЕМА ДИМЕТИЛ СУЛФОСИД + 1,4-ДИМЕТИЛБЕНЗЕН

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У овом раду дати су експериментални подаци за изотермску равнотежу пара–течност у опсегу температуре 303,15–333,15 K, као и густине, вискозности и индекса рефракције смеше диметил сулфоксида и 1,4-диметилбензена на температурама од 298,15 до 323,15 K, у комплетном опсегу састава смеше. Добијени PTX подаци корелисани су моделима Wilson и NRTL и процењени моделиом UNIFAC. Израчунате су вредности вишак Гибсове енергије и кофицијенти активности и упоређене са вредностима вишак других величина. Вишак моларне запремине и одступања вискозности и моларне рефракције израчунате су на основу експерименталних података; све израчунате величине фитоване су Redlich–Kister једначином. Добијене функције вишак величине тумачене су на основу структуре и интеракција молекула смеше.

(Примљено 25. новембра 2006, ревизирано 7. септембра 2007)

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