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# Molar Heat Capacities, Densities, Viscosities, and Refractive Indices of Dimethyl Sulfoxide + Tetrahydropyran and + 2-Methyltetrahydrofuran at (293.15, 303.15, and 313.15) K

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Molar heat capacities, $C_p$, densities, $\rho$, dynamic viscosities, $\eta$, and refractive indices, $n_D$, for the binary mixtures dimethyl sulfoxide (DMSO) + tetrahydropyran (THP) and + 2-methyltetrahydrofuran (MTHF) were determined at (293.15, 303.15, and 313.15) K using a Perkin-Elmer differential scanning calorimeter, an Anton Paar density meter, a Schott-Geräte AVS unit, and an Abbe refractometer, respectively. Excess molar volumes, $V_m^E$, deviations of the dynamic viscosities, $\Delta\eta$, and deviations of the refractive indices, $\Delta R$, were calculated at these temperatures. These properties were fitted to the Redlich−Kister equation.

## Introduction

Thermophysical and bulk properties of binary mixtures are very useful to obtain information on the intermolecular interactions and geometrical effects in the systems. Moreover, knowledge of the thermodynamic properties is essential for the proper design of industrial processes.

As a part of our research of investigating properties of binary mixtures containing dimethyl sulfoxide (DMSO),[1−5] in this paper we report molar heat capacities, $C_p$, densities, $\rho$, dynamic viscosities, $\eta$, and refractive indices, $n_D$, of the mixtures containing DMSO + two cyclic ethers, namely, tetrahydropyran (THP) and 2-methyltetrahydrofuran (MTHF), respectively. From them, excess molar volumes, $V_m^E$, deviations of the viscosities, $\Delta\eta$, and deviations of the refractive indices, $\Delta R$, were calculated. The measurements were carried out at atmospheric pressure and at (293.15, 303.15, and 313.15) K. In a previous paper, we have determined the molar heat capacities, $C_p$, of the DMSO + THP mixture but at 308.15 K, and to the best of our knowledge, we have found no references on these mixtures in the literature.

DMSO is a versatile, nonaqueous, dipolar, aprotic solvent with relative dielectric permittivity, $\epsilon = 46.45$, and a dipole moment at $\mu = 4.06$ D at 298.15 K.[6] DMSO was chosen because of its wide range of applicability as a solvent in chemical and biological processes, in pharmaceutical applications, in veterinary medicine, and in microbiology.[7−9] Moreover, several properties of this substance have gained attention in relation to cancer.[10] DMSO is also extensively used in kinetic studies[11] and in electrochemistry,[12] and it serves as a solvent for polymers.[13]

THP and MTHF, on the other hand, have relatively low values of relative permittivity and dipole moments. The thermodynamic properties of DMSO + THP and DMSO + MTHF should be related to the interactions between the S=O group provided by DMSO and the $-O-CH_3$ group of the two cyclic ethers.

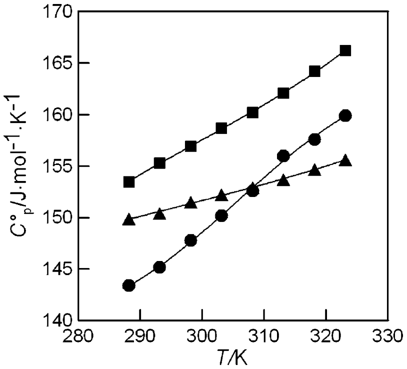

**Figure 1.** Heat capacities of pure components in the range (288.15 to 333.15) K. Full line, eq 1; ●, ▲, ■, refer to DMSO, THP, and MTHF, respectively.

Besides, THP and MTHF are isomeric cyclic ethers, which differ in the number of atoms in the carbon ring: MTHF has a ring of five carbon atoms instead of six and shows a less symmetrical structure due to the presence of a branching methyl group.

Our aim is to provide information about the molecular interaction in the liquid state and to compare the effect of this loss of symmetry in the excess and bulk properties of these mixtures.

## Experimental Section

***Materials.*** All compounds were purchased from Aldrich, showing an analytical grade of >99.7% for DMSO and >99% for both THP and MTHF. Liquids were used without further purification. Before use, the components were degassed by ultrasound (ultrasonic bath, Hellma, type 460, Milan, Italy) and dried over molecular sieves (Fluka, type 4A) to remove any traces of moisture. The purities of all compounds were corroborated by using a Hewlett-Packard G.CX. model 5890 supplied by an HP (cross-linked 5% ME siloxane) capillary column, and the obtained values complied with purchaser specifications.

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**Table 1. Densities, $\rho$, Dynamic Viscosities, $\eta$, Refractive Indices, $n_D$, Heat Capacities, $C_p$, of Pure Components and Comparison with Literature Values**

| | | $\rho$/g·cm$^{-3}$ | | $\eta$/mPa·s | | $n_D$ | | $C_p$/J·K$^{-1}$·mol$^{-1}$ | |
|---|---|---|---|---|---|---|---|---|---|
| component | $T$/K | this paper | lit. | this paper | lit. | this paper | lit. | this paper | lit. |
| DMSO | 293.15 | 1.10042 | 1.10041[a] | 2.213 | 2.2159[a] | 1.4815 | 1.47933[a]<br>1.4990[b] | 150.4 | |
| | 303.15 | 1.09041 | 1.09042[c] | 1.812 | 1.810[d] | 1.4750 | 1.4751[d] | 152.2 | |
| | 313.15 | 1.08026 | 1.08043[a] | 1.513 | 1.5126[d] | 1.4706 | 1.4707[d] | 153.7 | |
| THP | 293.15 | 0.88379 | 0.8814[a]<br>0.8849[e] | 0.875 | 0.826[a]<br>0.875[f] | 1.4235 | 1.42084[a] | 145.2 | |
| | 303.15 | 0.87395 | 0.8742[g] | 0.752 | | 1.4171 | 1.4159[g] | 150.2 | |
| | 313.15 | 0.86362 | 0.86380[h] | 0.658 | 0.6494[i] | 1.4119 | | 155.0 | 154.84[h] |
| MTHF | 293.15 | 0.85315 | 0.8540[a] | 0.492 | | 1.4085 | 1.40751[a] | 155.3 | |
| | 303.15 | 0.84280 | | 0.443 | | 1.4017 | | 158.6 | |
| | 313.15 | 0.83244 | 0.83365[j] | 0.416 | 0.410[k] | 1.3959 | | 162.1 | 161.56[h] |

[a] Ref 6. [b] Ref 14. [c] Ref 15. [d] Ref 16. [e] Ref 17. [f] Ref 18. [g] Ref 19. [h] Ref 20. [i] Ref 21. [j] Interpolated from ref 22. [k] Ref 23.

**Table 2. Experimental Liquid Heat Capacities, $C^0_p$, of Pure DMSO, THP, and MTHF at Atmospheric Pressure**

| | $C^0_p$/J·mol$^{-1}$·K$^{-1}$ | | |
|---|---|---|---|
| $T$/K | DMSO | THP | MTHF |
| 288.15 | 149.9 | 143.4 | 153.5 |
| 293.15 | 150.4 | 145.2 | 155.3 |
| 298.15 | 151.5 | 147.8 | 156.9 |
| 303.15 | 152.2 | 150.2 | 158.7 |
| 308.15 | 152.9 | 152.6 | 160.2 |
| 313.15 | 153.7 | 156.0 | 162.1 |
| 318.15 | 154.7 | 157.6 | 164.2 |
| 323.15 | 155.6 | 159.9 | 166.2 |

Experimental values of heat capacities, densities, viscosities, and refractive indices of the pure liquids are compared with available literature data[6,14−23] in Table 1.

***Heat Capacity Measurements.*** The heat capacity measurements, $C_p$, were determined by means of a Perkin-Elmer Pyris Diamond DSC differential scanning calorimeter equipped with a model ULSP 90 intra-cooler. The instrument was calibrated with high-purity standards (indium and cyclohexane) at 5 K·min$^{-1}$. The temperature was known to within ±0.1 K. The samples, approximately 10 mg, determined to ±0.01 mg, were encapsulated in hermetic pans. The heat capacity of the samples was obtained by means of three consecutive DSC runs at a scanning rate of 5 K·min$^{-1}$: the sample run, the blank run, and the standard sample (sapphire) run.[24] Care was taken to ensure that similar initial and final isotherm levels were reached for all three scans. The heat capacity data were obtained by means of the commercial software supplied by Perkin-Elmer. The estimated uncertainty for repeated data is less than 0.1%.

The experimental heat capacities, $C^0_p$, of pure components from (288.15 to 323.15) K vs the temperature $T$/K, at normal pressure, are listed in Table 2 and represented in Figure 1. The experimental values of the molar heat capacities, $C_p$, of mixtures vs the mole fraction, $x_1$, of DMSO are reported in Table 3 and represented in Figure 2. The expression used to fit $C^0_p$ as a function of temperature is

$$C^0_{\ p} = c_o + c_1(T/\mathrm{K}) + c_2(T/\mathrm{K})^2 \tag{1}$$

An analogous expression is used to fit $C_p$ as a function of $x_1$ at any temperature: $C^0_p$ and $T$/K in eq 1 are substituted by $C_p$ and $x_1$, respectively.

Values of the parameters $c_k$ are listed in Tables 4 and 5 together with the standard deviations $\sigma(C_p)$.

***Density Measurements.*** Excess molar volumes, $V^E_m$, reproducible to ±0.003 cm$^3$·mol$^{-1}$, have been determined from density measurements using a digital density meter (Anton Paar, model DMA 60, Graz, Austria) equipped with a measuring cell (Anton Paar, type 602) whose operating procedures have been described elsewhere.[25]

All measurements have been determined at a constant temperature using an external ultra-thermostat bath circulator (Heto, type 01 DTB 623, Birkeròd, Denmark), with a precision of ±0.005 K, and temperatures have been detected by a digital thermometer (Anton Paar, type CTK 100). Mole fractions, $x_1$, of DMSO (component 1) have been obtained by mass, using a digital balance (Mettler, model AE 160, Switzerland) with an accuracy of ±0.0001 g. All masses have been corrected for buoyancy and evaporation of components. Before each series of measurements, the apparatus was calibrated at atmospheric pressure using double-distilled water and dry air, whose densities were taken from the literature.[26,27] The uncertainty in density was ±1.5 × 10$^{-5}$ g·cm$^{-3}$. Correspondingly, the uncertainty in $V^E_m$ was estimated as <1 %.

Before measurements, the apparatus was checked by determining $V^E_m$ using the test mixture benzene + cyclohexane at 298.15 K. Our results agree with those of the literature[28] with a discrepancy of ±0.5 % in the central range of mole fraction of benzene.

The experimental results of the excess molar volumes, $V^E_m$, at atmospheric pressure and at (293.15, 303.15, and 313.15) K are listed in Table 6 as a function of the mole fraction $x_1$ and are graphically represented in Figure 3.

Density values of the mixtures, $\rho$, have been used to calculate the excess molar volumes, $V^E_m$, with the following equation:

$$V^E_m = (x_1M_1 + x_2M_2)/\rho - x_1M_1/\rho_1 - x_2M_2/\rho_2 \tag{2}$$

where $x_i$, $M_i$, and $\rho_i$ ($i$ = 1, 2) are the mole fractions, molecular weights, and densities of pure components 1 and 2, respectively.

***Viscosity Measurements.*** The kinematic viscosities, $\nu$, were determined using two Ubbelohde viscometers with a Schott-Geräte automatic measuring unit (model AVS 350), equipped with a thermostat (Lauda, model E 200, Germany) which provides temperature stabilization with an uncertainty of ±0.01 K. The capillary diameters of the two viscometers have values of (0.47 and 0.53) mm and were used for kinematic ranges of (0.5 to 0.8) mm$^2$·s$^{-1}$, respectively. The viscometers were filled with 15 cm$^3$ of solution for each measurement, and their calibration was carried out with double-distilled water and by a standard oil specimen of known viscosity. Quintuplicate measurements of flow times were reproducible within ±0.06 %. The uncertainty of the viscosity measurements was ±0.5 %.

The kinematic viscosities were calculated using the equation

$$\nu = \eta/\rho = k(t - \theta) \tag{3}$$

**Table 3. Experimental Molar Heat Capacities, $C_p$ (Equation 3), for Binary Mixtures Containing DMSO + THP and DMSO + MTHF**

| DMSO (1) + THP (2) | | | | DMSO (1) + MTHF (2) | | | |
|---|---|---|---|---|---|---|---|
| $x_1$ | $C_p$/J·mol$^{-1}$·K$^{-1}$ | $x_1$ | $C_p$/J·mol$^{-1}$·K$^{-1}$ | $x_1$ | $C_p$/J·mol$^{-1}$·K$^{-1}$ | $x_1$ | $C_p$/J·mol$^{-1}$·K$^{-1}$ |
| | | | | $T$/K = 293.15 | | | |
| 0.0996 | 148.8 | 0.5763 | 155.8 | 0.1033 | 155.2 | 0.6274 | 153.6 |
| 0.1317 | 149.7 | 0.6773 | 155.5 | 0.1368 | 155.1 | 0.6833 | 153.2 |
| 0.2636 | 153.0 | 0.7586 | 154.7 | 0.2714 | 155.0 | 0.7593 | 152.9 |
| 0.3636 | 154.6 | 0.8412 | 153.7 | 0.3775 | 154.6 | 0.8559 | 152.0 |
| 0.4832 | 155.9 | 0.9237 | 152.0 | 0.4881 | 154.2 | 0.9343 | 151.2 |
| 0.5309 | 156.0 | 0.9579 | 151.4 | 0.5877 | 153.8 | 0.9687 | 150.8 |
| | | | | $T$/K = 303.15 | | | |
| 0.0996 | 152.5 | 0.5763 | 156.5 | 0.1033 | 158.4 | 0.6274 | 155.8 |
| 0.1317 | 153.1 | 0.6773 | 156.0 | 0.1368 | 158.3 | 0.6833 | 155.4 |
| 0.2636 | 155.0 | 0.7586 | 155.5 | 0.2714 | 157.7 | 0.7593 | 154.7 |
| 0.3636 | 156.1 | 0.8412 | 154.6 | 0.3775 | 157.3 | 0.8558 | 153.8 |
| 0.4832 | 156.6 | 0.9237 | 153.2 | 0.4881 | 156.7 | 0.9343 | 152.9 |
| 0.5309 | 156.8 | 0.9579 | 152.9 | 0.5877 | 156.1 | 0.9687 | 152.7 |
| | | | | $T$/K = 313.15 | | | |
| 0.0996 | 157.1 | 0.5763 | 160.1 | 161.5 | 0.1033 | 0.6274 | 158.0 |
| 0.1317 | 157.7 | 0.6773 | 159.3 | 161.3 | 0.1368 | 0.6833 | 157.4 |
| 0.2636 | 159.3 | 0.7586 | 158.5 | 160.6 | 0.2714 | 0.7593 | 156.7 |
| 0.3636 | 160.0 | 0.8412 | 157.3 | 159.9 | 0.3775 | 0.8558 | 155.7 |
| 0.4832 | 160.5 | 0.9237 | 155.8 | 158.9 | 0.4881 | 0.9343 | 154.5 |
| 0.5309 | 160.3 | 0.9579 | 155.1 | 158.2 | 0.5877 | 0.9687 | 154.1 |

**Table 4. Adjustable Parameters of Equation 1 and Standard Deviation of Pure Components**

| component | $c_0$ | $c_1$ | $c_2$ | $\sigma(C_p)$/J·mol$^{-1}$·K$^{-1}$ |
|---|---|---|---|---|
| DMSO | 158.15 | −0.2003 | 0.0006 | 0.13 |
| THP | 82.566 | −0.0296 | 0.0008 | 0.17 |
| MTHF | 181.16 | −0.5004 | 0.0014 | 0.13 |

where $\eta$ is the absolute (dynamic) viscosity, $\rho$ is the density, $t$ is the flow time, $\theta$ is the kinetic energy correction, and $k$ is the viscometer constant, determined by calibration. In the whole set of experiments, flow times were maintained at >200 s, by selecting viscometers with appropriate values of $k$.

Equation 3 and the values of $\rho$ allow calculation of the deviation in viscosity, $\Delta\eta$, from the definition

$$\Delta\eta = \eta - \omega_1\eta_1 - \omega_2\eta_2 \tag{4}$$

where $\eta_k$ is the viscosity of the pure component $k$ and $\omega_k$ is its mass fraction in the mixture.

Deviations in viscosity, $\Delta\eta$, are represented in Figure 4.

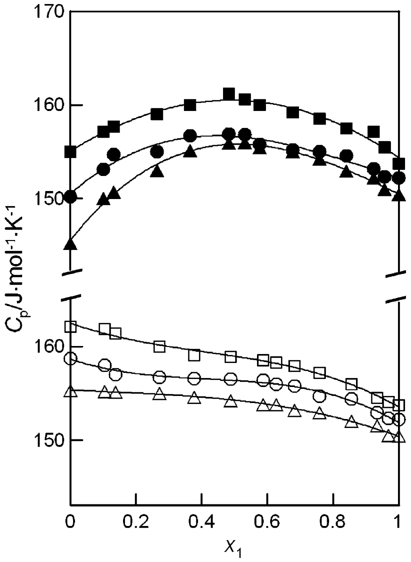

**Figure 2.** Molar heat capacities, $C_p$, for the binary mixtures DMSO (1) + THP (2) (full points) and DMSO (1) + MTHF (2) (open points). ▲, △, $T$/K = 293.15; ●, ○, $T$/K = 303.15; ■, □, $T$/K = 313.15; full line, eq 1.

**Table 5. Adjustable Parameters of Equation 1 and Standard Deviation of DMSO (1) + THP (2) and DMSO (1) + MTHF (2) at (293.15, 303.15, and 313.15) K**

| $T$/K | $c_0$ | $c_1$ | $c_2$ | $\sigma(C_p)$/J·mol$^{-1}$·K$^{-1}$ |
|---|---|---|---|---|
| | | DMSO (1) + THP (2) | | |
| 293.15 | 145.38 | 36.805 | −31.966 | 0.15 |
| 303.15 | 150.34 | 23.349 | −21.693 | 0.14 |
| 313.15 | 155.07 | 22.329 | −23.462 | 0.12 |
| | | DMSO (1) + MTHF (2) | | |
| 293.15 | 155.17 | 0.8928 | −5.521 | 0.11 |
| 303.15 | 158.62 | −1.563 | −4.775 | 0.07 |
| 313.15 | 161.97 | −3.711 | −4.477 | 0.11 |

***Refractive Indices Measurements.*** Refractive indices for the sodium D-line, $n_D$, were measured using a thermostatically controlled Abbe refractometer (Carl Zeiss, model G, Jena, Switzerland) with an accuracy of less than ±0.0001 units. A minimum of three independent readings was taken for each composition, and the average value was considered in all calculations. Water was circulated into the prism of the refractometer by a circulation pump connected to an external thermostated water bath. Calibration was performed by measuring the refractive indices of doubly distilled water, toluene, cyclohexane, and carbon tetrachloride at defined temperatures. The sample mixtures were directly injected into the prism assembly of the instrument using an airtight hypodermic syringe,

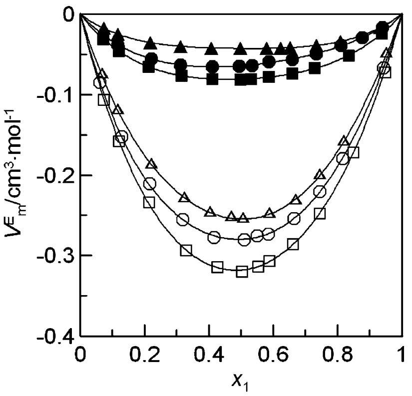

**Figure 3.** Excess molar volumes, $V^E_m$, for the binary mixtures DMSO (1) + THP (2) (full points) and DMSO (1) + MTHF (2) (open points). ▲, △, $T$/K = 293.15; ●, ○, $T$/K = 303.15; ■, □, $T$/K = 313.15; full line, eq 5.

**Table 6. Densities, $\rho$, Excess Molar Volumes, $V_m^E$, Dynamic Viscosities, $\eta$, Deviations in Dynamic Viscosities, $\Delta\eta$, Refracive Indices, $n_D$, and Deviations in Refractive Indices, $\Delta R$, of DMSO + THP and DMSO + MTHF at (293.15, 303.15, and 313.15) K**

| DMSO (1) + THP (2) | | | | | | | DMSO (1) + MTHF (2) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $x_1$ | $\rho$ g·cm$^{-3}$ | $V_m^E$ cm$^3$·mol$^{-1}$ | $\eta$ mPa·s | $\Delta\eta$ mPa·s | $n_D$ | $\Delta R$ cm$^3$·mol$^{-1}$ | $x_1$ | $\rho$ g·cm$^{-3}$ | $V_m^E$ cm$^3$·mol$^{-1}$ | $\eta$ mPa·s | $\Delta\eta$ mPa·s | $n_D$ | $\Delta R$ cm$^3$·mol$^{-1}$ |
| $T$/K = 293.15 | | | | | | | | | | | | | |
| 0.0730 | 0.89570 | −0.017 | 0.906 | −0.067 | 1.4268 | −0.080 | 0.0675 | 0.86578 | −0.075 | 0.537 | −0.070 | 1.4121 | −0.100 |
| 0.1171 | 0.90311 | −0.025 | 0.931 | −0.101 | 1.4288 | −0.126 | 0.1168 | 0.87528 | −0.120 | 0.561 | −0.131 | 1.4152 | −0.146 |
| 0.2176 | 0.92063 | −0.035 | 1.005 | −0.161 | 1.4336 | −0.212 | 0.2208 | 0.89602 | −0.187 | 0.631 | −0.239 | 1.4215 | −0.248 |
| 0.3108 | 0.93776 | −0.040 | 1.082 | −0.209 | 1.4383 | −0.274 | 0.3228 | 0.91754 | −0.229 | 0.719 | −0.327 | 1.4282 | −0.313 |
| 0.4069 | 0.95642 | −0.042 | 1.173 | −0.246 | 1.4433 | −0.318 | 0.4044 | 0.93566 | −0.247 | 0.780 | −0.386 | 1.4336 | −0.356 |
| 0.4982 | 0.97518 | −0.043 | 1.274 | −0.268 | 1.4483 | −0.339 | 0.4694 | 0.95078 | −0.253 | 0.876 | −0.421 | 1.4380 | −0.381 |
| 0.5786 | 0.99260 | −0.043 | 1.377 | −0.273 | 1.4528 | −0.347 | 0.5058 | 0.95950 | −0.255 | 0.926 | −0.433 | 1.4407 | −0.382 |
| 0.6227 | 1.00256 | −0.042 | 1.433 | −0.275 | 1.4554 | −0.342 | 0.5888 | 0.98016 | −0.248 | 1.047 | −0.455 | 1.4468 | −0.382 |
| 0.6527 | 1.00949 | −0.041 | 1.476 | −0.273 | 1.4573 | −0.331 | 0.6692 | 1.00125 | −0.231 | 1.194 | −0.446 | 1.4527 | −0.371 |
| 0.7338 | 1.02889 | −0.039 | 1.605 | −0.252 | 1.4624 | −0.296 | 0.7448 | 1.02204 | −0.200 | 1.354 | −0.415 | 1.4589 | −0.323 |
| 0.8085 | 1.04769 | −0.034 | 1.750 | −0.207 | 1.4673 | −0.245 | 0.8192 | 1.04357 | −0.158 | 1.550 | −0.347 | 1.4651 | −0.260 |
| 0.9321 | 1.08093 | −0.017 | 2.022 | −0.100 | 1.4761 | −0.109 | 0.9523 | 1.08475 | −0.049 | 2.004 | −0.121 | 1.4770 | −0.082 |
| $T$/K = 303.15 | | | | | | | | | | | | | |
| 0.1175 | 0.89340 | −0.038 | 0.804 | −0.073 | 1.4226 | −0.120 | 0.0609 | 0.85429 | −0.085 | 0.468 | −0.059 | 1.4055 | −0.064 |
| 0.2209 | 0.91149 | −0.056 | 0.865 | −0.122 | 1.4275 | −0.213 | 0.1281 | 0.86726 | −0.152 | 0.501 | −0.119 | 1.4096 | −0.137 |
| 0.3113 | 0.92813 | −0.063 | 0.925 | −0.157 | 1.4322 | −0.265 | 0.2161 | 0.88484 | −0.210 | 0.554 | −0.187 | 1.4152 | −0.211 |
| 0.4110 | 0.94752 | −0.066 | 1.001 | −0.187 | 1.4375 | −0.308 | 0.3184 | 0.90638 | −0.255 | 0.628 | −0.255 | 1.4216 | −0.295 |
| 0.4945 | 0.96464 | −0.064 | 1.078 | −0.198 | 1.4422 | −0.324 | 0.4156 | 0.92804 | −0.277 | 0.710 | −0.306 | 1.4281 | −0.346 |
| 0.5341 | 0.97308 | −0.064 | 1.112 | −0.206 | 1.4444 | −0.329 | 0.5105 | 0.95044 | −0.281 | 0.807 | −0.339 | 1.4349 | −0.364 |
| 0.5869 | 0.98464 | −0.059 | 1.168 | −0.206 | 1.4477 | −0.317 | 0.5491 | 0.95990 | −0.275 | 0.852 | −0.348 | 1.4378 | −0.363 |
| 0.6597 | 1.00127 | −0.056 | 1.250 | −0.201 | 1.4522 | −0.298 | 0.584 | 0.96873 | −0.273 | 0.896 | −0.353 | 1.4405 | −0.356 |
| 0.7348 | 1.01924 | −0.049 | 1.345 | −0.186 | 1.4571 | −0.257 | 0.6652 | 0.98997 | −0.254 | 1.013 | −0.348 | 1.4469 | −0.330 |
| 0.8105 | 1.03827 | −0.039 | 1.453 | −0.158 | 1.4621 | −0.205 | 0.7439 | 1.01162 | −0.221 | 1.149 | −0.321 | 1.4535 | −0.277 |
| 0.8760 | 1.05553 | −0.029 | 1.563 | −0.118 | 1.4666 | −0.143 | 0.8161 | 1.03251 | −0.179 | 1.286 | −0.283 | 1.4595 | −0.219 |
| 0.9393 | 1.07296 | −0.016 | 1.679 | −0.068 | 1.4710 | −0.072 | 0.9427 | 1.07155 | −0.067 | 1.623 | −0.121 | 1.4703 | −0.076 |
| $T$/K = 313.15 | | | | | | | | | | | | | |
| 0.7165 | 0.87538 | −0.031 | 0.681 | −0.038 | 1.4152 | −0.081 | 0.0723 | 0.84613 | −0.106 | 0.428 | −0.067 | 1.4004 | −0.082 |
| 0.1195 | 0.88344 | −0.046 | 0.701 | −0.059 | 1.4173 | −0.137 | 0.1209 | 0.85552 | −0.158 | 0.452 | −0.096 | 1.4034 | −0.134 |
| 0.2128 | 0.89976 | −0.065 | 0.745 | −0.060 | 1.4220 | −0.212 | 0.2135 | 0.87407 | −0.234 | 0.497 | −0.153 | 1.4093 | −0.219 |
| 0.3143 | 0.91844 | −0.076 | 0.803 | −0.124 | 1.4272 | −0.276 | 0.3285 | 0.89841 | −0.293 | 0.566 | −0.211 | 1.4117 | −0.296 |
| 0.4102 | 0.93709 | −0.081 | 0.863 | −0.146 | 1.4323 | −0.320 | 0.4268 | 0.92049 | −0.315 | 0.640 | −0.244 | 1.4237 | −0.347 |
| 0.4969 | 0.95493 | −0.081 | 0.927 | −0.156 | 1.4375 | −0.325 | 0.5020 | 0.93830 | −0.320 | 0.706 | −0.261 | 1.4291 | −0.366 |
| 0.5311 | 0.96223 | −0.081 | 0.953 | −0.159 | 1.4394 | −0.331 | 0.5525 | 0.95072 | −0.314 | 0.751 | −0.271 | 1.4330 | −0.362 |
| 0.5865 | 0.97436 | −0.078 | 0.997 | −0.162 | 1.4429 | −0.320 | 0.5881 | 0.95969 | −0.307 | 0.786 | −0.276 | 1.4357 | −0.359 |
| 0.6595 | 0.99106 | −0.074 | 1.063 | −0.159 | 1.4474 | −0.303 | 0.6613 | 0.97886 | −0.286 | 0.872 | −0.269 | 1.4415 | −0.339 |
| 0.7295 | 1.00780 | −0.067 | 1.136 | −0.146 | 1.4520 | −0.267 | 0.7441 | 1.00163 | −0.247 | 0.997 | −0.235 | 1.4484 | −0.290 |
| 0.8349 | 1.03454 | −0.051 | 1.260 | −0.112 | 1.4592 | −0.187 | 0.8488 | 1.03224 | −0.172 | 1.162 | −0.185 | 1.4572 | −0.205 |
| 0.9380 | 1.06250 | −0.024 | 1.405 | −0.056 | 1.4663 | −0.079 | 0.9474 | 1.06308 | −0.072 | 1.374 | −0.082 | 1.4666 | −0.079 |

**Table 7. Adjustable Parameters, $a_k$, from Equation 11 and Standard Deviations, $\sigma(Q)$ (Equation 5), of DMSO + THP and DMSO + MTHF at (293.15, 303.15, and 313.15) K**

| function | $T$/K | $a_0$ | $a_1$ | $a_2$ | $\sigma(Q)$ | function | $T$/K | $a_0$ | $a_1$ | $a_2$ | $\sigma(Q)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| DMSO (1) + THP (2) | | | | | | DMSO (1) + MTHF (2) | | | | | |
| $V_m^E$/cm$^3$·mol$^{-1}$ | 293.15 | −0.1709 | −0.0034 | −0.1201 | 0.0002 | $V_m^E$/cm$^3$·mol$^{-1}$ | 293.15 | −1.0184 | 0.0218 | −0.1832 | 0.0019 |
| | 303.15 | −0.2567 | 0.0622 | −0.1021 | 0.0005 | | 303.15 | −1.1208 | 0.0701 | −0.3016 | 0.0025 |
| | 313.15 | −0.3235 | 0.0328 | −0.1530 | 0.0004 | | 313.15 | −1.2728 | 0.0767 | −0.2657 | 0.0016 |
| $\Delta\eta$/mPa·s | 293.15 | −1.0702 | −0.3288 | −0.2434 | 0.0026 | $\Delta\eta$/mPa·s | 293.15 | −1.7348 | −0.7836 | −0.2372 | 0.0034 |
| | 303.15 | −0.8032 | −0.2537 | −0.1647 | 0.0016 | | 303.15 | −1.3426 | −0.6012 | −0.3303 | 0.0036 |
| | 313.15 | −0.6280 | −0.1890 | −0.1461 | 0.0013 | | 313.15 | −1.0484 | −0.3608 | −0.0019 | 0.0046 |
| $\Delta R$/cm$^3$·mol$^{-1}$ | 293.15 | −1.3679 | −0.2843 | −0.1062 | 0.0016 | $\Delta R$/cm$^3$·mol$^{-1}$ | 293.15 | −1.5299 | −0.2661 | −0.1825 | 0.0054 |
| | 303.15 | −1.3000 | −0.0995 | 0.1006 | 0.0025 | | 303.15 | −1.4512 | −0.1628 | 0.2521 | 0.0026 |
| | 313.15 | −1.3172 | −0.0711 | 0.0026 | 0.0031 | | 313.15 | −1.4464 | −0.2219 | 0.0554 | 0.0027 |

and an average of four measurements was taken for each mixture.

The solutions were pre-thermostated at the temperature of experience before the experiments to achieve a quick thermal equilibrium.

The molar refraction deviations, $\Delta R$, were calculated from the Lorentz−Lorenz equation, the same as that used in our previous papers,[2,3] and are represented in Figure 5.

The variation of $V_m^E$, $\Delta\eta$, and $\Delta R$ with composition is expressed by the Redlich−Kister polynomial

$$Q = x_1 x_2 \sum_{k \geq 0} a_k (x_1 - x_2)^k \tag{5}$$

where $Q$ refers to $V_m^E$, $\Delta\eta$, and $\Delta R$.

The adjustable parameters, $a_k$, were determined by a least-squares method, fitting the experimental values to eq 5, and the results are given in Table 7. The standard deviations, $\sigma(Q)$, reported in Table 7 are defined as

$$\sigma(Q) = |\phi_{\min}/(N - n)|^{0.5} \tag{6}$$

with $N$ and $n$ being the number of experimental points and parameters, respectively. $\phi_{\min}$ is the minimum value of the objective function $\phi$ defined as

$$\phi = \sum_{k=1}^{N} \eta_k^2 \tag{7}$$

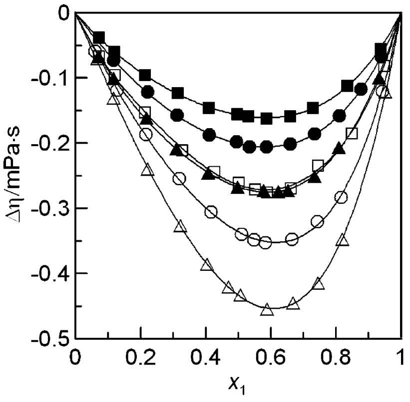

**Figure 4.** Experimental deviation in viscosities, $\Delta\eta$, for the binary mixtures DMSO (1) + THP (2) (full points) and DMSO (1) + MTHF (2) (open points). ▲, △, $T$/K = 293.15; ●, ○, $T$/K = 303.15; ■, □, $T$/K = 313.15; full line, eq 5.

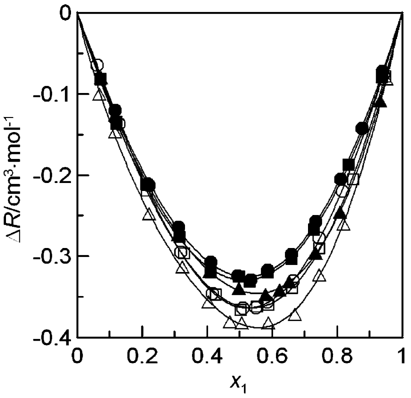

**Figure 5.** Deviation in refractive indices, $\Delta R$, for the binary mixtures DMSO (1) + THP (2) (full points) and DMSO (1) + MTHF (2) (open points). ▲, △, $T$/K = 293.15; ●, ○, $T$/K = 303.15; ■, □, $T$/K = 313.15; full line, eq 5.

where $\eta_k = Q_{\mathrm{calcd}} - Q$. $Q$ is the experimental value and $Q_{\mathrm{calcd}}$ is evaluated through eq 5.

## Results and Discussion

The figures indicate a general trend of properties in passing from THP to MTHF in a mixture with DMSO. Particularly, values of $C_p$, $V_m^E$, $\Delta\eta$, and $\Delta R$ for DMSO + THP are larger than the ones for DMSO + MTHF, with the smaller difference for $\Delta R$.

The viscosity data can be qualitatively explained by considering that the MTHF isomer has a branching $CH_3$ group, leading to packing of molecules in the pure state that is more loose than that with THP and a consequent lower density and larger mobility (lower viscosity) of the structure (see Table 1).

This smaller viscosity is enhanced in mixtures with DMSO (see Table 6) because, most probably, interaction of MTHF with DMSO (dipole−dipole interaction) is less with respect to THP, due to the steric hindrance of $CH_3$.

Analogously, the presence of a $CH_3$ group in MTHF implies less density of pure MTHF and a relatively lower variation of $\rho$ in going from pure components to mixtures of TMHF + DMSO.

Increasing the temperature leads to an increase of $\Delta\eta$ and a decrease of $V_m^E$ for mixtures of both THP and MTHF with DMSO.

The values of $C^0_p$ of pure DMSO are slightly higher than those we previously obtained with a different apparatus[2,3] and are very close to the values reported by Becker and Gmehling,[29] in the same range of temperatures.

Values of $C_p$ increase with increasing temperature, and mixtures of DMSO + THP show a maximum of $C_p$ as a function of the mole fraction.

## Literature Cited

(1) Comelli, F.; Ottani, S.; Francesconi, R.; Castellari, C. Excess Molar Enthalpies of Binary Mixtures Containing Glycols or Polyglycols + Dimethyl Sulfoxide at 308.15 K. *J. Chem. Eng. Data* **2003**, *48*, 995−998.

(2) Francesconi, R.; Bigi, A.; Rubini, K.; Comelli, F. Excess Enthalpies, Heat Capacities, Densities, Viscosities, and Refractive Indices of Dimethyl Sulfoxide + Three Aryl Alcohols at 308.14 K and Atmospheric Pressure. *J. Chem. Eng. Data* **2005**, *50*, 1932−1937.

(3) Comelli, F.; Francesconi, R.; Bigi, A.; Rubini, K. Excess Molar Enthalpies, Molar Heat Capacities, Densities, Viscosities, and Refractive Indices of Dimethyl Sulfoxide + Esters of Carbonic Acid at 308.15 K and at Atmospheric Pressure. *J. Chem. Eng. Data* **2006**, *51*, 665−670.

(4) Francesconi, R.; Comelli, F.; Bigi, A.; Rubini, K. Thermophysical Properties of Dimethyl Sulfoxide + Cyclic and Linear Ethers at 308.15 K. Application of an Extended Cell Model. *Thermochim. Acta* **2006**, *447*, 154−160.

(5) Comelli, F.; Francesconi, R.; Bigi, A.; Rubini, K. Excess Molar Enthalpies, Molar Heat Capacities, Densities, Viscosities, and Refractive Indices of Dimethyl Sulfoxide + 1-Propanol at (288.15, 298.15, and 308.15) K and at Normal Pressure. *J. Chem. Eng. Data* **2006**, *51*, 1711−1716.

(6) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Wiley-Interscience: New York, 1986.

(7) Pasha, M. K.; Dimmock, J. R.; Hollenberg, M. D.; Sharma, R. K. Enhanced Activity of Human *N*-Myristoyltransferase by Dimethyl Sulfoxide and Related Solvents in the Presence of Serine/Threonine-Containing Peptide Substrates. *Biochem. Pharmacol.* **2002**, *64*, 1461−1467.

(8) Sweetman, S. C. *Martindale, the Complete Drug Reference,* 33rd ed.; Pharmaceutical Press: London, 2002.

(9) *The Merck Index,* 13th ed.; Merck & Co., Inc.: Whitehouse Station, NJ, 2001.

(10) Salim, A. Removing Oxygen-derived Free Radicals Delays Hepatic Metastases and Prolongs Survival in Colonic Cancer. *Oncology* **1992**, *49*, 58−62.

(11) Hou, C.; Ji, C.; Qu, R.; Wang, Chu.; Wang, Che. Kinetics of Copolymerizazion and Degradation of Poly[acrylonitrile-*co*-(amino ethyl-2-methyl ptopenoate)]. *Eur. Polym. J.* **2006**, *42*, 1093−1098

(12) Yuan, D.; Liu, Y. Electrochemical Preparation La-Co Magnetic Alloy Films from Dimethylsulfoxide. *Mater. Chem. Phys.* **2006**, *96*, 79−83.

(13) Yeo, S-D.; Kiran, E. Formation of Polymer Particles with Supercritical Fluids: A Review. *J. Supercrit. Fluids* **2005**, *34*, 287−308.

(14) Shen, J.-L.; Li, Z.-F.; Wang, B.-H.; Zhang, Y.-M. Partial Molar Volumes of Some Amino Acids and a Peptide in Water, DMSO, NaCl, and DMSO/NaCl Aqueous Solutions. *J. Chem. Thermodyn.* **2000**, *32*, 805−820

(15) Ruostesuo, P.; Pirilae-Honkanen, P. Thermodynamic and Spectroscopic Properties of 2-Pyrrolidones. Dielectric Properties of 2-Pyrrolidone in Binary Mixtures. *J. Solution Chem.* **1990**, *19*, 473−482.

(16) Bicknell, R. T. M.; Davies, D. B.; Lawrence, K. G. Density, Refractive Index, Viscosity and 1H Nuclear Magnetic Resonance Measurements of Dimethyl Sulfoxide at 2 °C Intervals in the Range 20−60 °C. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 1595−1602.

(17) Whitehead, E. V.; Dean, R. A.; Fidler, F. A. The Preparation and Physical Properties of Sulfur Compounds Related to Petroleum. II. Cyclic Sulfides. *J. Am. Chem. Soc.* **1951**, *73*, 3632−3635.

(18) Kuss, L. High Pressure Research. III. The Viscosity of Compressed Liquids. *Z. Angew. Phys.* **1955**, *7*, 372−378.

(19) Moelwyn-Huges, E. A.; Thorpe, D. L. The Physical and Thermodynamic Properties of Some Associated Solutions. I. Dielectric Constants and Heats of Mixing. *Proc. Roy. Soc. (London)* **1964**, *277*, 423−436.

(20) Rodriguez, S.; Lafuente, C.; Artigas, H.; Royo, F. M.; Urieta, J. S. Densities, Speeds of Sound, and Isentropic Compressibilities of a Cyclic Ether with Chlorocyclohexane, or Bromocyclohexane at the Temperature 298.15 K and 313.15 K. *J. Chem. Thermodyn.* **1999**, *31*, 139−149.

(21) Pèrez, E.; Mainar, A. M.; Santafè, J.; Urieta, J. S. Excess Enthalpy, Excess Volume, Viscosity deviation, and Speed of Sound Deviation for the Mixture Tetrahydropyran + 2,2,2-Trifluoroethanol at (283.15 and 313.15) K. *J. Chem. Eng. Data* **2003**, *48*, 723−726.

(22) De Lorenzi, L.; Fermeglia, M.; Torriano, G. Density and Viscosity of 1-Methoxy-2-propanol, 2-Methyltetrahydrofuran, α,α,α-Trifluoroethane, and Their Binary Mixtures with 1,1,1-Trichloroethane at Different Temperatures. *J. Chem. Eng. Data* **1996**, *41*, 1121−1125.

(23) De Lorenzi, L.; Fermeglia, M.; Torriano, G. Densities and Viscosities of 1,1,1-Trichloroethane with 13 Different Solvents at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 1172−1177.

(24) O'Neill, M. J. Measurement of specific heat functions by differential scanning calorimetry. *Anal. Chem.* **1966**, *38*, 1331.

(25) Fermeglia, M.; Lapasin, J. Excess Volumes and Viscosities of Binary Mixtures of Organics. *J. Chem. Eng. Data* **1988**, *33*, 415−417.

(26) Kohlrausch, F. Density of Air. *Prakt. Phys.* **1968**, *3*, 40.

(27) Wagenbreth, H.; Blanke, W. Die Dichte des Wassers im Internationalen Einheitensystem und in die Internationalen Practishen Temperaturskala von 1968. PTB: Mitteilungen. 1971; Vol. *6/71*, p 412.

(28) Wilhelm, E. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1985**, 164.

(29) Becker, L.; Gmehling, J. Measurement of Heat Capacities for 12 Organic Substances by Tian−Calvet Calorimetry. *J. Chem. Eng. Data* **2001**, *46*, 1638−1642.

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