# Densities, Viscosities, Refractive Indices, and Surface Tensions of Dimethyl Sulfoxide + Butyl Acetate Mixtures at (293.15, 303.15, and 313.15) K

**Nikos G. Tsierkezos, Antonis E. Kelarakis, and Maria M. Palaiologou***

Physical Chemistry Laboratory, Department of Chemistry, University of Athens, P.O. Box 64004,
157 10 Zografou, Athens, Greece

---

Densities ($\rho$), viscosities ($\eta$), refractive indices ($n_D$), and surface tensions ($\sigma$) have been measured for dimethyl sulfoxide + butyl acetate mixtures, over the entire composition range at (293.15, 303.15, and 313.15) K. The excess volumes ($V^E$), the viscosity deviations ($\Delta\eta$), and the deviations in refraction ($\Delta R$) were calculated from these experimental data. All the properties have negative values. The results have been fitted to the Redlich−Kister type polynomial relation, and the corresponding parameters have been derived. The results are discussed in terms of molecular interactions.

---

## Introduction

Continuing our work on solution properties (Palaiologou and Molinou, 1995; Palaiologou, 1996; Tsierkezos and Molinou, 1998; Tsierkezos and Molinou, 1999), we present in this paper experimental data on the density, viscosity, refractive index, and surface tension of binary mixtures of dimethyl sulfoxide (DMSO) + butyl acetate at (293.15, 303.15, and 313.15) K. From these results the excess volumes, viscosity deviations, and deviations in refraction have been derived.

Dimethyl sulfoxide is a versatile nonaqueous dipolar aprotic solvent having the relative dielectric constant $\epsilon = 46.6$ and the dipole moment $\mu = 3.90$ D at 298.15 K. It is extensively used in kinetic studies and electrochemistry and serves as a solvent for polymers. Butyl acetate is a very good solvent for polymers too. The study of the thermodynamic properties of DMSO + butyl acetate mixtures is of interest in industrial fields, where solvent mixtures could be used as selective solvents for polymers.

The excess properties of binary liquid mixtures containing DMSO have been studied previously (Cowie and Toporowski, 1961; Fort and Moore, 1966; Pruett and Felker, 1985; Aminabhavi and Gopalakrishna, 1995; Nikam et al., 1996). Densities and viscosities of binary mixtures of butyl acetate with aromatic hydrocarbons (Iloukhani et al., 1984; Qin et al., 1992), xylenes (Ramachandran et al., 1995), methylacetoacetate (Aminabhavi et al., 1993), diethylene glycol dimethyl ether (Aminabhavi et al., 1993), 4-methyl-2-pentanone (Fermeglia et al., 1990), and nitroethane (Liu et al., 1999) are reported in the literature.

A survey in the literature showed that dimethyl sulfoxide + butyl acetate mixtures have not been studied.

## Experimental Section

***Materials.*** The reagents, dimethyl sulfoxide (Riedel-de Haën, >99.9%) and butyl acetate (Merck p.a., >99.5%) were used without further purification. The purity of the liquids was assessed by comparing the experimental densities, viscosities, 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 error in mole fraction is <±0.0001.

***Measurements.*** A digital densimeter (Anton Paar, model DMA 58) was used for the determination of the densities of the pure components and the binary mixtures. The estimated uncertainty of the measured densities is $\pm 0.000\ 01\ \text{g}\cdot\text{cm}^{-3}$. The DMA cell was calibrated with dry air and doubly-distilled water at atmospheric pressure. The sample volume was 0.7 $\text{cm}^3$, and the sample thermostat was controlled to ±0.01 K.

The flow times of the mixtures and the pure liquids were measured in a Schott Geräte AVS 310 unit, equipped with an Ubbelohde capillary viscometer. The viscometer was calibrated with conductivity water. The time measurement tolerance was ±0.005%, and the display accuracy was ±0.01 s. The viscometer was placed in a thermostat (model Schott CT 050/2) electronically controlling the set temperature. The temperature was maintained constant within ±0.03 K. The accuracy in the viscosity measurements was ±0.001 mPa·s.

The refractive indices at the sodium D-line were measured with a thermostated Abbe refractometer (model A. Krüss) with a built-in light source for the measuring prism with an accuracy of ±0.0001. The thermostat temperature was constant ±0.01 K.

Surface tensions were measured by detachment of a platinum ring using a temperature-controlled (±0.2 K) surface tensiometer (Kruss, Model K8600). The ring was washed successively with dilute HCl and water. The tensiometer was calibrated with distilled water, and the correction factor was employed. The accuracy of the surface tension measurement was $\pm 0.1\ \text{mN}\cdot\text{m}^{-1}$.

## Results and Discussion

The experimental values of density, viscosity, and refractive index at (293.15, 303.15, and 313.15) K are given in Table 2.

10.1021/je990271t CCC: $19.00

**Table 1. Comparison of Experimental Densities ($\rho$), Viscosities ($\eta$), and Refractive Indices ($n_D$) of Pure Liquids with Literature Values**

| $T$/K | $\eta$(exp)/ mPa·s | $\eta$(ref)/ mPa·s | $\rho$(exp)/ g·cm$^{-3}$ | $\rho$(ref)/ g·cm$^{-3}$ | $n_D$(exp) | $n_D$(ref) |
|---|---|---|---|---|---|---|
| | | | Dimethyl Sulfoxide | | | |
| 293.15 | 2.244 | | 1.100 53 | 1.100 50$^{a}$ | 1.4795 | 1.4776$^{a}$ |
| 303.15 | 1.830 | 1.788$^{b}$ | 1.090 49 | 1.090 50$^{b}$ | 1.4752 | |
| 313.15 | 1.534 | | 1.080 32 | 1.080 46$^{c}$ | 1.4700 | |
| | | | Butyl Acetate | | | |
| 293.15 | 0.735 | 0.7279$^{e}$ | 0.881 45 | 0.881 65$^{d}$<br>0.881 45$^{e}$ | 1.3947 | 1.3939$^{e}$ |
| 303.15 | 0.648 | 0.6361$^{e}$<br>0.634$^{h}$ | 0.871 09 | 0.870 96$^{e}$<br>0.871 34$^{f}$<br>0.871 27$^{g}$<br>0.870 50$^{h}$ | 1.3902 | 1.3911$^{h}$ |
| 313.15 | 0.565 | 0.5617$^{e}$<br>0.557$^{h}$ | 0.860 67 | 0.860 64$^{e}$<br>0.860 00$^{h}$ | 1.3858 | 1.3864$^{h}$ |

[a] Korosi and Kovats (1981). [b] Nikam et al. (1996). [c] Pruett and Felker (1985). [d] Qin et al. (1992). [e] Liu et al. (1999). [f] Iloukhani et al. (1984). [g] Ramachandran et al. (1995). [h] Aminabhavi et al. (1993).

**Table 2. Experimental Densities ($\rho$), Viscosities ($\eta$), and Refractive Indices ($n_D$) of Dimethyl Sulfoxide (1) + Butyl Acetate (2) Mixtures**

| $x_1$ | $\rho$/g·cm$^{-3}$ | $\eta$/mPa·s | $n_D$ | $x_1$ | $\rho$/g·cm$^{-3}$ | $\eta$/mPa·s | $n_D$ |
|---|---|---|---|---|---|---|---|
| | | | $T$ = 293.15 K | | | | |
| 0.0000 | 0.881 45 | 0.735 | 1.3947 | 0.5427 | 0.968 77 | 1.211 | 1.4286 |
| 0.0510 | 0.887 78 | 0.774 | 1.3974 | 0.6419 | 0.991 07 | 1.363 | 1.4376 |
| 0.1000 | 0.894 50 | 0.789 | 1.3995 | 0.7402 | 1.015 98 | 1.527 | 1.4471 |
| 0.2052 | 0.909 17 | 0.868 | 1.4056 | 0.8611 | 1.051 43 | 1.791 | 1.4607 |
| 0.3643 | 0.934 67 | 1.011 | 1.4154 | 0.9565 | 1.084 00 | 2.063 | 1.4724 |
| 0.4408 | 0.948 49 | 1.098 | 1.4208 | 1.0000 | 1.100 53 | 2.244 | 1.4795 |
| | | | $T$ = 303.15 K | | | | |
| 0.0000 | 0.871 09 | 0.648 | 1.3902 | 0.5427 | 0.959 08 | 1.032 | 1.4244 |
| 0.0510 | 0.877 71 | 0.678 | 1.3929 | 0.6419 | 0.981 18 | 1.146 | 1.4331 |
| 0.1000 | 0.884 21 | 0.692 | 1.3950 | 0.7402 | 1.005 97 | 1.280 | 1.4429 |
| 0.2052 | 0.898 95 | 0.752 | 1.4010 | 0.8611 | 1.041 96 | 1.488 | 1.4566 |
| 0.3643 | 0.924 66 | 0.879 | 1.4111 | 0.9565 | 1.074 12 | 1.697 | 1.4689 |
| 0.4408 | 0.938 60 | 0.931 | 1.4164 | 1.0000 | 1.090 49 | 1.830 | 1.4752 |
| | | | $T$ = 313.15 K | | | | |
| 0.0000 | 0.860 67 | 0.565 | 1.3858 | 0.5427 | 0.949 11 | 0.889 | 1.4203 |
| 0.0510 | 0.867 56 | 0.592 | 1.3884 | 0.6419 | 0.971 46 | 0.983 | 1.4286 |
| 0.1000 | 0.874 01 | 0.606 | 1.3906 | 0.7402 | 0.996 72 | 1.117 | 1.4385 |
| 0.2052 | 0.888 76 | 0.662 | 1.3967 | 0.8611 | 1.031 93 | 1.258 | 1.4524 |
| 0.3643 | 0.914 77 | 0.766 | 1.4068 | 0.9565 | 1.064 13 | 1.423 | 1.4648 |
| 0.4408 | 0.928 66 | 0.809 | 1.4121 | 1.0000 | 1.080 32 | 1.534 | 1.4700 |

**Table 3. Parameters of Eq 6 and Standard Deviations ($d$) of Excess Functions of Dimethyl Sulfoxide (1) + Butyl Acetate (2) Mixtures**

| function | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $d$ |
|---|---|---|---|---|---|
| | | $T$ = 293.15 K | | | |
| $V^E$/cm$^3$·mol$^{-1}$ | −0.7795 | −0.0538 | −0.1456 | 0.0633 | 0.0102 |
| $\Delta\eta$/mPa·s | −1.2974 | −0.4942 | −0.4986 | −0.4456 | 0.0074 |
| $\Delta R$/cm$^3$·mol$^{-1}$ | −6.6888 | 2.1316 | −0.8994 | −0.2082 | 0.0121 |
| | | $T$ = 303.15 K | | | |
| $V^E$/cm$^3$·mol$^{-1}$ | −1.0031 | −0.0609 | −0.2719 | −0.0547 | 0.0163 |
| $\Delta\eta$/mPa·s | −0.9889 | −0.3923 | −0.3250 | −0.2018 | 0.0062 |
| $\Delta R$/cm$^3$·mol$^{-1}$ | −6.7636 | 2.0823 | −0.7680 | 0.2048 | 0.0097 |
| | | $T$ = 313.15 K | | | |
| $V^E$/cm$^3$·mol$^{-1}$ | −1.2914 | −0.3251 | −0.4821 | 0.4926 | 0.0186 |
| $\Delta\eta$/mPa·s | −0.7569 | −0.2420 | −0.2183 | −0.2947 | 0.0106 |
| $\Delta R$/cm$^3$·mol$^{-1}$ | −6.8228 | 1.9879 | −0.4768 | 0.8724 | 0.0097 |

The excess molar volumes, $V^E$, were calculated from the experimental data according to the following equation:

$$V^E = V_m - \sum_{i=1}^{2} V_i x_i \tag{1}$$

where $x_i$ and $V_i$ represent the mole fraction and the molar volume of the $i$th pure component, respectively, and $V_m$, the molar volume of the mixture, can be calculated from the following equation:

$$V_m = \sum_{i=1}^{2} x_i \mathrm{M}_i / \rho_m \tag{2}$$

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

The viscosity deviations, $\Delta\eta$, were calculated from the following equation:

$$\Delta\eta = \eta_m - \sum_{i=1}^{2} \eta_i x_i \tag{3}$$

where $\eta_i$ and $\eta_m$ represent the viscosity of the $i$th pure component and that of the mixture, respectively.

The refractive index deviations, $\Delta R$, were obtained from the Lorentz−Lorenz (Lorentz, 1909) equation

$$\Delta R = R_m - \sum_{i=1}^{2} R_i \varphi_i \tag{4}$$

where $R_i$ and $R_m$ are the molar refraction of the $i$th component and that of the mixture, respectively, and $\varphi_i$ is the volume fraction of the $i$th component, given as

$$\varphi_i = x_i V_i / \sum_{i=1}^{2} x_i V_i \tag{5}$$

The calculation of molar refraction $R_i$ and $R_m$ was reported in a previous paper (Tsierkezos and Molinou, 1998).

The experimental values of $V^E$, $\Delta\eta$ , and $\Delta R$ were fitted to the Redlich−Kister equation (Redlich and Kister, 1948)

$$Y = x_1 x_2 \sum_{k=0}^{n} A_k (2x_1 - 1)^k \tag{6}$$

where $Y$ represents the excess volume, the viscosity deviations, or the deviations in refraction and $A_k$ represents the parameters. A nonlinear least-squares method was used to estimate the parameters $A_k$. The optimum number of parameters was obtained through examination of the standard deviation, $d$, according to the equation

$$d = \left[\frac{\Sigma(Y_{\mathrm{expt}} - Y_{\mathrm{calcd}})^2}{(n - p)}\right]^{1/2} \tag{7}$$

where $n$ is the total number of data points and $p$ is the number of estimated parameters. The values of $A_k$ and $d$ are presented in Table 3.

Plots of excess molar volume at (293.15, 303.15, and 313.15) K versus mole fraction of DMSO are shown in Figure 1. For all mixtures the values of $V^E$ are negative, indicating specific interactions between DMSO and butyl acetate molecules. There is a decrease of the $V^E$ with increasing temperature.

The viscosity deviations versus the mole fraction of DMSO are plotted in Figure 2. The $\Delta\eta$ values are negative through the entire composition range and for all temperatures investigated, and they increase with a rise in temperature.

The deviations in refractive indices are shown in Figure 3. The $\Delta R$ values are negative for the whole composition range for all mixtures. The values are independent of temperature, as predicted by the theory, and the molar refraction depends only on the wavelength of light used for measurement (Glasstone, 1965).

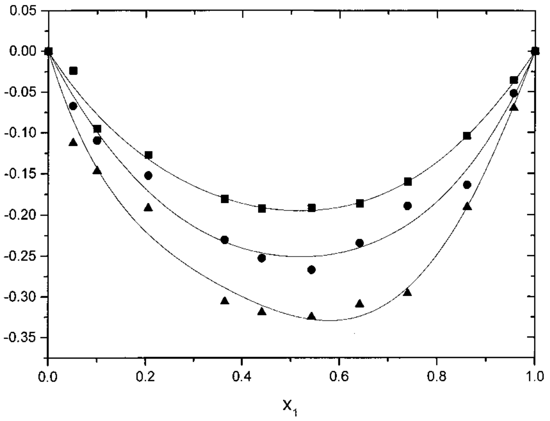

**Figure 1.** Excess molar volumes for dimethyl sulfoxide (1) + butyl acetate (2) mixtures at 293.15 (■), 303.15 (●), and 313.15 K (▲).

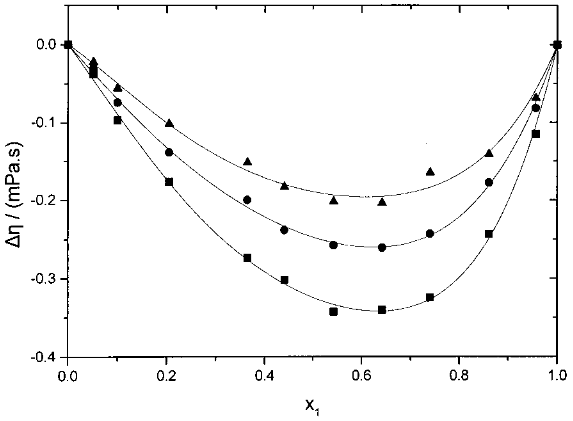

**Figure 2.** Viscosity deviations of dimethyl sulfoxide (1) + butyl acetate (2) mixtures at 293.15 (■), 303.15 (●), and 313.15 K (▲).

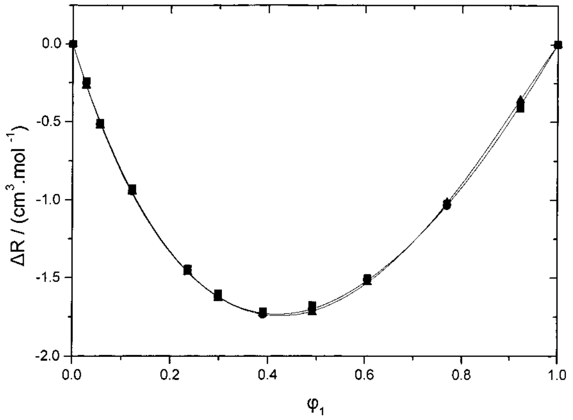

**Figure 3.** Molar refraction deviations of dimethyl sulfoxide (1) + butyl acetate (2) mixtures versus the volume fraction of dimethyl sulfoxide at 293.15 (■), 303.15 (●), and 313.15 K (▲).

The surface tension values ($\sigma$) for the binary mixtures of DMSO + butyl acetate are given in Table 4. The surface tension of the binary mixtures was increased as the DMSO concentration was increased too. This trend is nonlinear, the change in surface tension being larger at high DMSO concentrations than that at low concentrations.

Connors and Wright (1989) propose an equation of the form

$$\sigma = \sigma_2 - \left(1 + \frac{a x_2}{1 - \beta x_2}\right) x_1 (\sigma_2 - \sigma_1) \qquad (8)$$

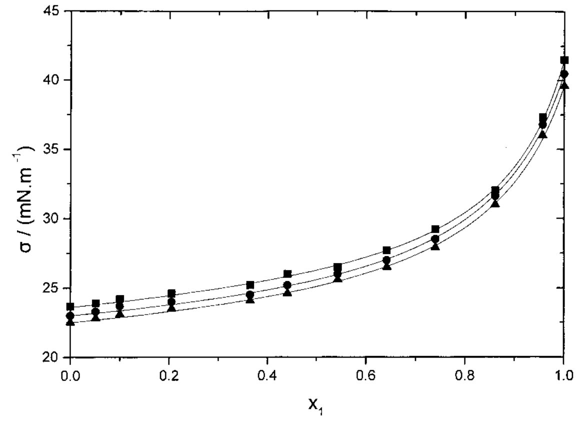

**Figure 4.** Surface tension for dimethyl sulfoxide (1) + butyl acetate (2) mixtures at 293.15 (■), 303.15 (●), and 313.15 K (▲).

**Table 4. Surface Tension ($\sigma$) of Dimethyl Sulfoxide (1) + Butyl Acetate (2) Mixtures**

| | $\sigma$/mN·m$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| $T$/K | $x_1$ = 0.0000 | $x_1$ = 0.0510 | $x_1$ = 0.1000 | $x_1$ = 0.2052 | $x_1$ = 0.3643 | $x_1$ = 0.4408 |
| 293.15 | 23.6 | 23.9 | 24.2 | 24.6 | 25.2 | 26.0 |
| 303.15 | 23.0 | 23.3 | 23.7 | 24.0 | 24.5 | 25.2 |
| 313.15 | 22.5 | 22.8 | 23.1 | 23.5 | 24.1 | 24.6 |

| | $\sigma$/mN·m$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| $T$/K | $x_1$ = 0.5427 | $x_1$ = 0.6419 | $x_1$ = 0.7402 | $x_1$ = 0.8611 | $x_1$ = 0.9565 | $x_1$ = 1.000 |
| 293.15 | 26.5 | 27.7 | 29.2 | 32.0 | 37.3 | 41.5 |
| 303.15 | 26.0 | 27.0 | 28.5 | 31.6 | 36.8 | 40.5 |
| 313.15 | 25.6 | 26.5 | 27.9 | 31.0 | 36.0 | 39.6 |

**Table 5. Surface Tension Parameters α and $\beta$ (Eq 8) for Dimethyl Sulfoxide (1) + Butyl Acetate (2) Mixtures**

| $T$/K | α | $\beta$ |
|---|---|---|
| 293.15 | −6.301 | −6.994 |
| 303.15 | −5.469 | −5.772 |
| 313.15 | −5.417 | −5.790 |

where $\sigma_2$, $\sigma_1$, and $\sigma$ are the surface tensions of butyl acetate, DMSO, and the mixture, respectively, to describe the effect of composition on the mixture surface tension. The parameters α and $\beta$ are given in Table 5. The values of $\sigma$ versus the mole fraction of dimethyl sulfoxide are shown in Figure 4.

In the systems studied, surface tension decreased with increasing temperature for any given mole fraction of DMSO.

## Literature Cited

Aminabhavi, T. M.; Gopalakrishna, B. Density, Viscosity, Refractive Index, and Speed of Sound in Aqueous Mixtures of N,N-Dimethylformamide, Dimethyl Sulfoxide, N,N-Dimethylacetamide, Acetonitrile, Ethylene Glycol, Diethylene Glycol, 1,4-Dioxane, Tetrahydrofuran, 2-Methoxyethanol, and 2-Ethoxyethanol at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 856−861.

Aminabhavi, T. M.; Phayde, H. T. S.; Khinnavar, R. S.; Bindu, G. Densities, Refractive Indices, Speeds of Sound, and Viscosities of Diethylene Glycol Dimethyl Ether + Butyl Acetate at 298.15, 303.15, 308.15, 313.15, and 318.15 K. *J. Chem. Eng. Data* **1993a**, *38*, 542−545.

Aminabhavi, T. M.; Raikar, S. K.; Balundgi, R. H. Densities, Viscosities, Refractive Indices, and Speeds of Sound in Methyl Acetoacetate + Methyl Acetate, + Ethyl Acetate, + *n*-Butyl Acetate, + Methyl Benzoate, and + Ethyl Benzoate at 298.15, 303.15, and 308.15 K. *J. Chem. Eng. Data* **1993b**, *38*, 441−445.

Connors, A. K.; Wright, L. J. Dependence of Surface Tension on Concentration of Binary aqueous−Organic Solutions. *Anal. Chem.* **1989**, *61*, 194−198.

Cowie, J. M. G.; Toporowski, P. M. Association in the Binary Liquid System Dimethyl Sulfoxide−Water. *Can. J. Chem.* **1961**, *39*, 2240−2243.

Fermeglia, M.; Lapasin, R.; Torriano, G. Excess Volumes and Viscosities of Binary Systems Containing 4-Methyl-2-Pentanone. *J. Chem. Eng. Data* **1990**, *35*, 260−265.

Fort, R. J.; Moore, W. R. Viscosities of Binary Liquid Mixtures. *J. Chem. Soc., Faraday Trans.* **1966**, *62*, 1112−1119.

Glasstone, S. *Textbook of Physical Chemistry*; MacMillan: London, 1965.

Iloukhani, H.; Reddy, K. D.; Prabhakara Rao, M. V. Excess Volumes of the Binary Mixtures of Substituted Benzenes with Ethyl Acetate and Butyl Acetate. *J. Chem. Eng. Data* **1984**, *29*, 474−476.

Korosi, G,; Kovats, E. Sz. Density and Surface Tension of 83 Organic Liquids. *J. Chem. Eng. Data* **1981**, *26*, 323−332.

Liu, C.-Y.; Ku, H.-C.; Tu, C.-H. Densities and Viscosities of Five Alkyl Esters with Nitroethane Systems at (293.15, 303.15, and 313.15) K. *J. Chem. Eng. Data* **1999**, *44*, 360−364.

Lorentz, H. A. *Theory of Electrons*; Teubner: Leipzig, 1909.

Nikam, P. S.; Jadhav, M. C.; Hasan, M. Density and Viscosity of Mixtures of Dimethyl Sulfoxide + Methanol, + Ethanol, + Propan-1-ol, + Propan-2-ol, + Butan-1-ol, + 2-Methylpropan-1-ol, and 2-Methylpropan-2-ol at 298.15 K and 303.15 K. *J. Chem. Eng. Data* **1996**, *41*, 1028−1031.

Palaiologou, M. M. Densities, Viscosities, and Refractive Indices of Some Alkyl Esters with 4-Chlorotoluene Systems at 293.15, 298.15, and 303.15 K. *J. Chem. Eng. Data* **1996**, *41*, 1036−1039.

Palaiologou, M. M.; Molinou, I. E. Excess Volumes of Ethyl Acetate + Toluene, + *o*-Chlorotoluene, and + *p*-Chlorotoluene from 283.15 to 303.15 K. *J. Chem. Eng. Data* **1995**, *40*, 880−882.

Pruett, D. J.; Felker, L. K. Densities and Apparent Molar Volumes in the Binary System Dimethyl Sulfoxide−Water at 25, 40, 60, and 65 °C. *J. Chem. Eng. Data* **1985**, *30*, 452−455.

Qin, A.; Hoffman, D. E.; Munk, P. Excess Volume of Mixtures of Selected Alkyl Esters and Ketones with Aromatic Hydrocarbons. *J. Chem. Eng. Data* **1992**, *37*, 66−70.

Ramachandran, D.; Rambabu, K.; Krishnan, K. M.; Venkateswarlu, P.; Raman, G. K. Volume of Mixing, Speed of Sound, and Viscosity of Butyl Acetate with Xylenes at 303.15 K. *J. Chem. Eng. Data* **1995**, *40*, 815−817.

Redlich, O.; Kister, A. T. *Ind. Eng. Chem.* **1948**, *40*, 345.

Tsierkezos, N. G.; Molinou, I. E. Thermodynamic Properties of Water + Ethylene Glycol at 283.15, 293.15, 303.15, and 313.15 K. *J. Chem. Eng. Data* **1998**, *43*, 989−993.

Tsierkezos, N. G.; Molinou, I. E. Densities and Viscosities of Ethylene Glycol Binary Mixtures at 293.15 K. *J. Chem. Eng. Data* **1999**, *44*, 955−958.

Received for review October 5, 1999. Accepted January 4, 2000.

JE990271T