1028 *J. Chem. Eng. Data* **1996,** *41,* 1028−1031

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

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Densities and viscosities have been measured for the binary 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. From these results, the excess molar volume (V^E) and deviation in viscosity ($\Delta\eta$) have been computed. These properties are used to calculate regression coefficients of the Redlich−Kister equation.

Introduction

Studies on excess functions of binary liquid mixtures are of considerable importance in understanding the nature of molecular interactions. Several investigations have already been carried out to get insight into the nature and degree of interactions that are present in liquid mixtures using excess properties (Marsh et al., 1984; Aralaguppi et al., 1991; Comelli and Francesconi, 1995).

Dimethyl sulfoxide (DMSO) is a versatile nonaqueous dipolar aprotic solvent having relative dielectric constant $\epsilon = 46.50$ and dipole moment $\mu = 4.06$ at 298.15 K. It is extensively used in kinetic studies and electrochemistry and serves as a solvent for polymers. On the other hand, alkanols are the most well-known solvents used to study the hydrophobic effects. Thermodynamic properties of DMSO + alkanol mixtures are of interest because DMSO provides an >S═O group and alkanols provide an OH group for interactions. To determine the extent and type of interactions between DMSO and alkanol molecules, the densities and viscosities of binary mixtures of DMSO with alkanols have been measured.

Experimental Section

The alkanols used were of 99.7% purity (E. Merk). They were dried by refluxing with fused calcium oxide for 5 h and then fractionally distilled two to three times (Riddick et al., 1986). Dimethyl sulfoxide (S. D. Fine Chemicals, 99.5%) was purified by distilling it over activated charcoal at a reduced pressure (Martin and Hauthal, 1975). Purities as determined by gas−liquid chromatography were better than 99.8 mol % for all the liquids. Their density (ζ) and viscosity (η) values compared well with the literature data (Table 1).

All mixtures were prepared by mass using a Mettler balance (Switzerland, model AE-240) with a precision of ±0.01 mg. Mixtures were allowed to stand for some time before every measurement so as to avoid air bubbles. The possible error in mole fraction is estimated to be less than $\pm 1 \times 10^{-4}$.

Densities of pure liquids and their mixtures were determined by using a 15 cm^3 double arm pycnometer as described earlier (Nikam and Hasan, 1988; Nikam et al., 1995a,b). The pycnometer was calibrated using conductivity water with 0.997 05 g·cm^{-3} as its density at 298.15 K. The pycnometer filled with air bubble free experimental liquids was kept in a transparent-walled water bath (maintained constant to ±0.01 K) for 10 to 15 min to attain thermal equilibrium. The positions of the liquid levels in the two arms were recorded with the help of a traveling microscope which could be read to ±0.01 mm. The density values were reproducible to within 1×10^{-4} g·cm^{-3}.

Table 1. Comparison of Densities, ζ, and Viscosities, η, of Pure Components with Literature Data at 298.15 K

	ζ/g·cm^{-3}		η/mPa·s	
component	exptl	lit. (Riddick et al., 1986)	exptl	lit. (Riddick et al., 1986)
methanol	0.7868	0.786 37	0.557	0.5513
ethanol	0.7854	0.784 93	1.079	1.0826
propan-1-ol	0.7996	0.799 60	1.934	1.9430
propan-2-ol	0.7816	0.781 26	2.045	2.0436
butan-1-ol	0.8067	0.805 75	2.568	2.5710
2-methylpropan-1-ol	0.7987	0.799 80	3.334	3.3330
2-methylpropan-2-ol	0.7809	0.781 20	4.439	4.438
dimethyl sulfoxide	1.0959	1.095 37	1.991	1.991

The viscosity of the binary liquid mixtures was measured using an Ostwald viscometer calibrated with water with 0.8937 mPa·s as its viscosity at 298.15 K. A thoroughly cleaned and dried viscometer, filled with experimental liquid, was placed vertically in a glass-sided water thermostat maintained constant to ±0.01 K. After thermal equilibrium was attained, the efflux times of flow of liquids were recorded with a digital stopwatch correct to ±0.01 s. Since all flow times were greater than 300 s, the kinetic energy corrections were found to be negligible. The data presented in Table 2 are the averages of at least three independent measurements. The accuracy in the measurement of viscosity was ±0.001 mPa·s. The other experimental details of the measurements of viscosity are the same as described previously (Nikam and Hasan, 1992; Nikam et al., 1994, 1995a).

Results and Discussion

The experimental results for the density (ζ) are given in Table 2. The excess volume, V^E, was calculated from

$$V^E = \frac{M_1x_1 + M_2x_2}{\zeta_{12}} - \frac{M_1x_1}{\zeta_1} - \frac{M_2x_2}{\zeta_2} \qquad (1)$$

where ζ_{12} is the density of the mixture and M_1, x_1, ζ_1 and M_2, x_2, ζ_2 are the molecular weight, mole fraction, and

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Table 2. Density (ζ) and Viscosity (η) for Dimethyl Sulfoxide (DMSO) (1) + Alkanols (2) at 298.15 K and 303.15 K

	T = 298.15 K		T = 303.15 K			T = 298.15 K		T = 303.15 K	
x_1	ζ/g·cm^{-3}	η/mPa·s	ζ/g·cm^{-3}	η/mPa·s	x_1	ζ/g·cm^{-3}	η/mPa·s	ζ/g·cm^{-3}	η/mPa·s
				DMSO + Methanol					
0.0000	0.7868	0.557	0.7818	0.523	0.4902	0.9923	1.030	0.9873	0.937
0.0439	0.8127	0.583	0.8078	0.544	0.6224	1.0255	1.259	1.0210	1.110
0.0930	0.8406	0.616	0.8351	0.566	0.7858	1.0602	1.564	1.0550	1.368
0.1279	0.8560	0.642	0.8530	0.583	0.8923	1.0796	1.768	1.0738	1.573
0.2139	0.8978	0.708	0.8927	0.661	0.9667	1.0913	1.923	1.0856	1.713
0.2908	0.9288	0.792	0.9233	0.741	1.0000	1.0959	1.991	1.0906	1.788
0.3809	0.9592	0.884	0.9546	0.820					
				DMSO + Ethanol					
0.0000	0.7854	1.079	0.7811	0.987	0.5814	0.9855	1.298	0.9813	1.201
0.0616	0.8102	1.015	0.8052	0.966	0.7023	1.0204	1.454	1.0153	1.354
0.1286	0.8355	1.021	0.8312	0.932	0.7609	1.0361	1.538	1.0309	1.481
0.2019	0.8622	1.022	0.8582	0.884	0.8414	1.0571	1.657	1.0523	1.562
0.2801	0.8898	1.056	0.8859	0.904	0.9330	1.0798	1.851	1.0744	1.685
0.3708	0.9203	1.114	0.9165	0.938	1.0000	1.0955	1.991	1.0903	1.788
0.4693	0.9516	1.187	0.9479	1.064					
				DMSO + Propan-1-ol					
0.0000	0.7996	1.934	0.7963	1.731	0.5363	0.9575	1.562	0.9528	1.436
0.0789	0.8227	1.750	0.8192	1.630	0.6421	0.9889	1.641	0.9842	1.495
0.1613	0.8467	1.651	0.8430	1.540	0.7550	1.0226	1.736	1.0179	1.570
0.2478	0.8722	1.581	0.8681	1.452	0.8737	1.0579	1.845	1.0533	1.676
0.3390	0.8991	1.535	0.8948	1.399	1.0000	1.0960	1.991	1.0905	1.788
0.4340	0.9272	1.541	0.9227	1.389					
				DMSO + Propan-2-ol					
0.0000	0.7816	2.049	0.7805	1.781	0.5347	0.9419	1.501	0.9398	1.346
0.0788	0.8041	1.742	0.8024	1.576	0.6423	0.9762	1.597	0.9742	1.406
0.1608	0.8280	1.589	0.8257	1.447	0.7546	1.0128	1.679	1.0105	1.505
0.2475	0.8536	1.473	0.8513	1.358	0.8737	1.0525	1.828	1.0498	1.622
0.3389	0.8812	1.475	0.8786	1.319	1.0000	1.0954	1.991	1.0904	1.788
0.4347	0.9107	1.451	0.9082	1.315					
				DMSO + Butan-1-ol					
0.0000	0.8067	2.568	0.8024	2.262	0.5874	0.9595	1.770	0.9547	1.599
0.0944	0.8286	2.225	0.8243	1.970	0.6887	0.9886	1.796	0.9835	1.625
0.1920	0.8522	2.017	0.8478	1.848	0.7915	1.0237	1.859	1.0167	1.668
0.2893	0.8568	1.880	0.8723	1.671	0.8839	1.0549	1.905	1.0495	1.723
0.3876	0.9028	1.780	0.8981	1.604	1.0000	1.0960	1.990	1.0905	1.788
0.4688	0.9235	1.773	0.9188	1.590					
				DMSO + 2-Methylpropan-1-ol					
0.0000	0.7987	3.333	0.7946	2.881	0.5874	0.9530	1.853	0.9483	1.592
0.0944	0.8205	2.785	0.8163	2.424	0.6887	0.9851	1.858	0.9801	1.686
0.1917	0.8440	2.366	0.8398	2.071	0.7913	1.0194	1.891	1.0142	1.693
0.2890	0.8687	2.056	0.8645	1.847	0.8951	1.0564	1.918	1.0508	1.733
0.3884	0.8953	1.934	0.8909	1.754	1.0000	1.0955	1.991	1.0902	1.788
0.4863	0.9229	1.879	0.9183	1.703					
				DMSO + 2-Methylpropan-2-ol					
0.0000	0.7809	4.439	0.7752	3.378	0.5873	0.9400	2.005	0.9349	1.459
0.0950	0.8037	3.564	0.7977	2.644	0.6888	0.9742	1.917	0.9692	1.531
0.1916	0.8280	2.968	0.8218	2.111	0.7916	1.0112	1.902	1.0065	1.568
0.2890	0.8527	2.530	0.8473	1.808	0.8951	1.0513	1.971	1.0465	0.719
0.3874	0.8794	2.269	0.8747	1.608	1.0000	1.0949	1.990	1.0907	1.788
0.5132	0.9165	2.070	0.9115	1.479					

density of pure components 1 and 2, respectively. Excess volumes calculated from eq 1 are listed in Table 2.

Results of V^E were fitted to a Redlich−Kister (1948) polynomial equation

$$V^E/\mathrm{cm}^3\cdot\mathrm{mol}^{-1} = x_1x_2\sum_{i=0}^{m}a_i(x_2 - x_1)^i \qquad (2)$$

where m is the number of coefficients a_i. In each case, the optimum number of coefficients is ascertained from an examination of the variation in standard deviation, σ, as given by

$$\sigma = [\sum(Y_{\mathrm{obsd}} - Y_{\mathrm{calcd}})^2/(n - m)]^{1/2} \qquad (3)$$

where n is the total number of data points and m is the number of coefficients considered. The coefficients and standard deviations for V^E as computed from eqs 2 and 3, respectively, are given in Table 3.

The experimental results for the viscosity (η) are also given in Table 2. The viscosity deviations, $\Delta\eta$, are obtained by

$$\Delta\eta/\mathrm{mPa\cdot s} = \eta_{12} - x_1\eta_1 - x_2\eta_2 \qquad (4)$$

where η_{12} is the viscosity of the mixture and x_1, η_1 and x_2, η_2 are the mole fraction and viscosity of pure components 1 and 2, respectively.

The coefficients, a_i, and standard deviation, σ, for $\Delta\eta$ as obtained from equations similar to eqs 2 and 3 are listed in Table 3.

A comparison is made of observed excess molar volumes and deviations in viscosity of dimethyl sulfoxide−methanol binary mixtures at 298.15 K with those reported in literature (Wei and Rowley, 1984). The deviations (δ) in

Table 3. Parameters and Standard Deviations, *σ*, of Eqs 2 and 3 for DMSO + Alkanols

system		T/K	a_0	a_1	a_2	a_3	σ
DMSO + methanol	$V^E/\mathrm{cm^3\cdot mol^{-1}}$	298.15	−2.527	1.555	−0.916	−1.128	0.018
		303.15	−2.730	−1.268	−0.292	−0.252	0.013
	$\Delta\eta/\mathrm{mPa\cdot s}$	298.15	−0.880	0.173	0.148	−0.055	0.005
		303.15	−0.794	−0.058	0.147	0.029	0.008
DMSO + ethanol	$V^E/\mathrm{cm^3\cdot mol^{-1}}$	298.15	−1.457	−0.051	−0.591	0.550	0.012
		303.15	−1.771	0.515	0.174	0.551	0.012
	$\Delta\eta/\mathrm{mPa\cdot s}$	298.15	−1.250	−0.103	−0.491	0.656	0.010
		303.15	−1.217	1.101	0.255	−1.123	0.015
DMSO + propanol-1-ol	$V^E/\mathrm{cm^3\cdot mol^{-1}}$	298.15	−0.885	0.040	0.106	0.278	0.005
		303.15	−0.739	−0.118	0.342	0.049	0.005
	$\Delta\eta/\mathrm{mPa\cdot s}$	298.15	−1.600	0.522	−0.337	0.416	0.012
		303.15	−1.392	0.599	0.301	−0.431	0.007
DMSO + propanol-2-ol	$V^E/\mathrm{cm^3\cdot mol^{-1}}$	298.15	0.515	−0.116	0.027	−0.182	0.002
		303.15	−0.381	4.651	5.922	−18.787	0.023
	$\Delta\eta/\mathrm{mPa\cdot s}$	298.15	−2.106	0.945	−0.924	0.920	0.016
		303.15	−1.802	0.666	−0.455	0.194	0.004
DMSO + butan-1-ol	$V^E/\mathrm{cm^3\cdot mol^{-1}}$	298.15	−0.297	−0.092	−0.144	−0.094	0.004
		303.15	−0.307	−0.093	−0.190	0.084	0.004
	$\Delta\eta/\mathrm{mPa\cdot s}$	298.15	−2.028	0.922	−0.524	0.413	0.007
		303.15	−1.732	0.645	−0.300	0.600	0.025
DMSO + 2-methylpropan-1-ol	$V^E/\mathrm{cm^3\cdot mol^{-1}}$	298.15	0.294	−0.106	−0.327	−0.231	0.004
		303.15	0.287	0.003	−0.021	−0.082	0.004
	$\Delta\eta/\mathrm{mPa\cdot s}$	298.15	−3.222	2.246	−0.604	−0.934	0.014
		303.15	−2.599	1.769	−0.643	−0.501	0.012
DMSO + 2-methylpropan-2-ol	$V^E/\mathrm{cm^3\cdot mol^{-1}}$	298.15	1.220	0.143	−1.372	0.983	0.008
		303.15	1.023	0.403	−0.162	−0.217	0.016
	$\Delta\eta/\mathrm{mPa\cdot s}$	298.15	−4.578	2.144	−0.994	0.982	0.021
		303.15	−5.157	1.913	1.165	1.254	0.025

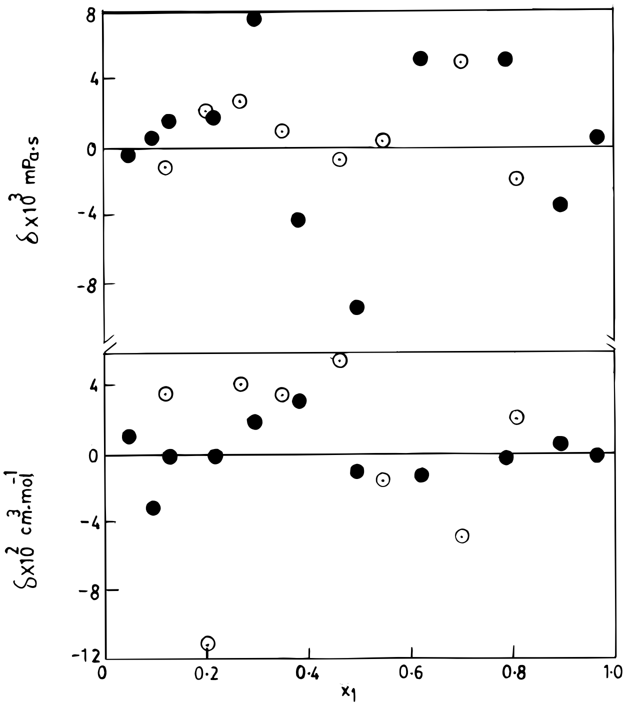

Figure 1. Deviations, δ, from eq 5 for the DMSO (1)−methanol (2) System at 298.15 K: (⊙) Wei and Rowley; (●) this work.

V^E and $\Delta\eta$ were calculated from the following equation

$$\delta(Y) = Y_{\mathrm{exptl}} - Y_{\mathrm{cald}} \qquad (5)$$

Where Y is either V^E or $\Delta\eta$.

In Figure 1, deviation plots for V^E and $\Delta\eta$ are given. Our results compare well with those reported in the literature (Wei and Rowley, 1984).

Excess molar volumes (V^E) are negative for mixtures of DMSO with methanol, ethanol, propan-1-ol, and butan-1-ol and are positive for mixtures of DMSO with propan-2-ol, 2-methylpropan-1-ol, and 2-methylpropan-2-ol) (Figure 2). The V^E values at equimolar concentrations of DMSO and alkanols in mixtures follow the trend methanol < ethanol < propan-1-ol < butan-1-ol < 2-methylpropan-1-ol < propan-2-ol < 2-methylpropan-2-ol.

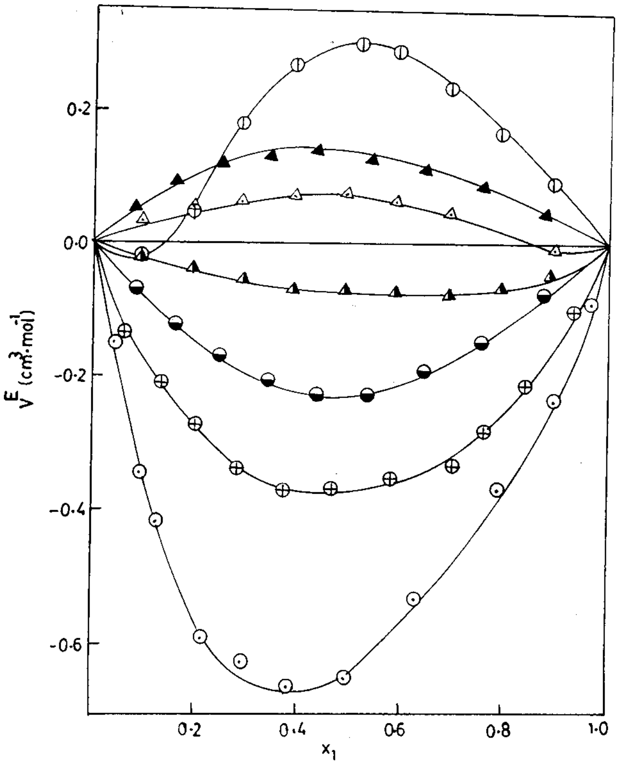

Figure 2. Excess molar volumes, V^E, at 298.15 K for x_1DMSO + $(1 - x_1)$alkanols: (⊙) methanol; (⊕) ethanol; (◒) propan-1-ol; (▲) propan-2-ol; (△) butan-1-ol; (△) 2-methylpropan-1-ol; (⦶) 2-methylpropan-2-ol.

The observed excess molar volumes may be discussed in terms of physical, chemical, and geometrical contributions (Aminabhavi et al., 1993). The physical interactions involve mainly dispersion forces, giving a positive contribution to V^E. The chemical or specific interactions between constituent molecules of the mixture result in a volume

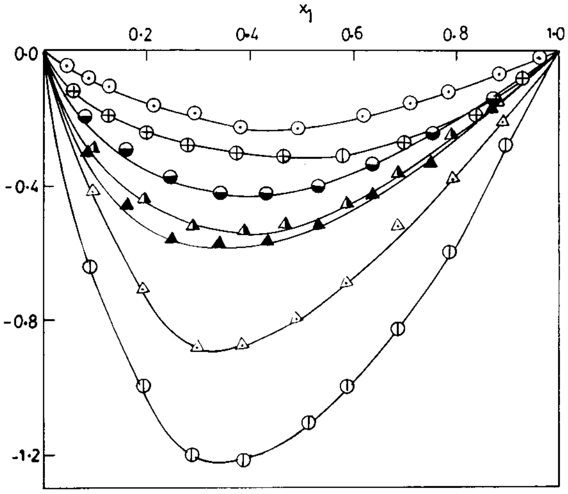

Figure 3. $\Delta\eta$ values at 298.15 K for x_1DMSO + (1 − x_1)alkanols: (⊙) methanol; (⊕) ethanol; (◒) propan-1-ol; (▲) propanol-2-ol; (◭) butan-1-ol; (△) 2-methylpropan-1-ol; (⦶) 2-methylpropan-2-ol.

decrease. In the present investigation, a specific interaction between alkanol and DMSO molecules takes place through dipole−dipole interaction, forming the complex through hydrogen bond formation. The structural contribution arising from the geometrical fitting of one component into the other, due to differences in the molar volumes and free volumes between components leads to negative contributions to V^E (Aminabhavi et al., 1993). Since the molecular dynamics of these species is complicated, it is difficult to attribute the observed V^E values to geometrical fitting of one component into another. With higher alkanols the clustering decreases with an increase in chain length and branching of alkanols (Mecke, 1950). Therefore the mixtures containing higher and branched alkanols give larger V^E values as compared to those containing lower and straight chain alkanols.

The $\Delta\eta$ values of mixtures of DMSO with alkanols are negative (Figure 3). $\Delta\eta$ values at equimolar concentrations of DMSO−alkanol mixtures follow the trend methanol > ethanol > propan-1-ol > butan-1-ol > propan-2-ol > 2-methylpropan-1-ol > 2-methylpropan-2-ol. The viscosity changes ($\Delta\eta$) of DMSO−alkanol mixtures are essentially due to two factors: (i) the depolymerization of the associated entities like DMSO and alkanols to monomeric moieties on mixing, which leads to a negative contribution to $\Delta\eta$, and (ii) replacement of like contacts in pure alkanols and DMSO by unlike contacts, which is responsible for positive values.

Therefore it seems that the depolymerization process outweighs the formation of unlike contacts in these mixtures, leading to negative $\Delta\eta$ values. Since higher or branched alkanols are less associated, mixtures of DMSO with higher or branched alkanols give more negative values.

In the present work, the V^E and $\Delta\eta$ values are not significantly affected at the temperatures of measurements.

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Received for review January 29, 1996. Revised manuscript received April 15, 1996. Accepted June 6, 1996.[⊗]

JE9600358

[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1996.