J. Chem. Eng. Data **2006,** *51,* 1711−1716

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

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Excess molar enthalpies, molar heat capacities, densities, viscosities, and refractive indices of dimethyl sulfoxide + 1-propanol have been measured at (288.15, 298.15, and 308.15) K and at normal pressure using an LKB microcalorimeter, a Perkin-Elmer differential scanning calorimeter, an Anton Paar density meter, a Schott-Geräte AVS unit, and an Abbe refractometer, respectively. Heat capacities of 1-propanol have been determined in the range $288.15 < T/\mathrm{K} < 333.15$. The results were fitted to the Redlich−Kister polynomial equation to obtain the adjustable parameters and standard deviations.

Introduction

In previous papers,[1−3] we reported experimental excess thermodynamic and bulk properties for binary mixtures containing dimethyl sulfoxide (DMSO) as a common component. The present article continues this work, reporting excess molar enthalpies, H_m^E, molar heat capacities, C_p^E, densities, ρ, viscosities, η, and refractive index, n, and various derived properties of DMSO + 1-propanol at (288.15, 298.15, and 308.15) K and at normal pressure.

The aim of the study of this mixture is to acquire information on the behavior of the mixture from structural and energetic considerations. Dimethylsulfoxide (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.[4−6] Moreover, several properties of this substance have gained attention in relation to cancer.[7] DMSO is a highly polar aprotic solvent because of its S═O group and has a large dipole moment and relative permittivity (μ = 4.06 D and ϵ = 46.45 at 298.15 K, respectively).[8] 1-Propanol, on the other hand, has relatively lower values of relative permittivity (ϵ = 20.l45) and dipole moment ((μ = 3.09) than those of DMSO. Therefore, thermodynamic properties of the binary mixture DMSO + 1-propanol are of interest because DMSO provides an S═O group and propanol provides an OH group for interactions. The effect of varying the temperature on the mixture has been studied.

For the mixture DMSO + 1-propanol, the literature reports values of excess enthalpy at 298.15 K,[9,10] values of density and viscosity at (298.15 and 303.15) K[11] and at 308.15 K.[12]

Experimental Section

Materials. DMSO, analytical grade >99.5 %, was purchased from Fluka, while 1-propanol, analytical grade >99.9 %, was obtained from Aldrich. Both 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 (Aldrich, type 3A) to remove any traces of moisture. Purities of all products were checked 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.

Experimental values of densities, viscosities, refractive indices, and heat capacities of the pure components were compared with literature data,[8,13−20] as shown in Table 1.

Calorimetric Measurements. A flow-type isothermal microcalorimeter (LKB, model 2107, Producer AB, Bromma, Sweden) was used in this study to measure the excess molar enthalpy. The apparatus consists of a flow mixing cell, a reference cell, a thermostatic water bath, a data acquisition unit, and two liquid burets (ABU Radiometer, Copenhagen, Denmark). The water bath controls the temperature of the heat sink where the mixing cell, reference cell, and thermoelectric sensors are placed. The temperature of the bath is maintained constant to within ±0.01 K. The pure components are pumped into the mixing cell at selected flow rates. The component mass fractions in the mixed stream were obtained from densities and volumetric flow rates of components 1 (DMSO) and 2 (1-propanol). The total flow rates are usually kept at about 0.4 $\mathrm{cm^3 \cdot min^{-1}}$ which is a preferable condition as a results of test runs. However, in dilute regions of DMSO or 1-propanol, the total flow rates may increase up to 0.8 $\mathrm{cm^3 \cdot min^{-1}}$. The uncertainties of mole fraction of each run were estimated to be less than ±0.001 in mole fraction. Details and operating procedure of the apparatus have been reported elsewhere.[21,22] The uncertainties of the reported H_m^E values in this study were verified by measurements on three standard systems, cyclohexane + hexane, benzene + cyclohexane, and methanol + water at 298.15 K, known in the literature.[23] Agreement with literature data is better than 0.5 % at the maximum of the thermal effect.

The H_m^E values were determined from the following relationship

$$H_m^E = [I^2 R(E/E_c)]/f \qquad (1)$$

where I and R are the electrical current and resistance in the

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10.1021/je0601513 CCC: $30.25

Table 1. Densities, ρ, Dynamic Viscosities, η, Refractive Indices, n_D, and Heat Capacities, C_p, of Pure Components and Comparison with Literature Values

		ρ/g·cm^{-3}		η/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	288.15	1.10539		2.473		1.4835		146.8	
	298.15	1.09536	1.09537[a]	1.989	1.991[a]	1.4778	1.47754[a]	152.4	153.18[a]
	308.15	1.08531	1.0854[b]	1.644	1.636[b]	1.4730	1.4729[c]	154.6	
	308.15				1.652[d]				
1-propanol	288.15	0.80751	0.80749[a]	2.498	2.492[a]	1.3893	1.39178[e]	139.0	
	288.15						1.38719[f]		
	298.15	0.79954	0.79960[a]	1.952	1.943[a]	1.3837	1.3837[a]	144.9	143.87[a]
	308.15	0.79141	0.7913[g]	1.564	1.565[h]	1.3795	1.3792[i]	151.2	

[a] Reference 8. [b] Reference 13. [c] Reference 14. [d] Reference 15. [e] Reference 16. [f] Reference 17. [g] Reference 18. [h] Reference 19. [i] Reference 20.

Table 2. Excess Molar Enthalpies, H^E_m, for Binary Mixtures Containing DMSO + 1-Propanol at (288.15, 298.15, and 308.15) K

	H^E_m		H^E_m		H^E_m
x_1	J·mol^{-1}	x_1	J·mol^{-1}	x_1	J·mol^{-1}
T/K = 288.15					
0.0420	215	0.3449	818	0.8456	389
0.0807	375	0.4124	822	0.8634	344
0.1163	493	0.5129	792	0.8939	283
0.1493	581	0.6124	724	0.9267	204
0.2084	701	0.6781	661	0.9619	111
0.2598	760	0.7595	537		
T/K = 298.15					
0.0422	207	0.3456	831	0.8086	464
0.0809	366	0.4131	839	0.8638	357
0.1166	491	0.5137	810	0.8942	282
0.1497	589	0.6131	732	0.9269	206
0.2089	697	0.6787	671	0.9621	111
0.2604	762	0.7602	561		
T/K = 308.15					
0.0421	212	0.3454	829	0.8084	465
0.0808	365	0.4128	833	0.8636	343
0.1234	509	0.5134	807	0.8941	292
0.1495	586	0.6120	733	0.9268	205
0.2087	698	0.6784	668	0.9620	113
0.2601	765	0.7599	541		

electrical calibration experiments, E and E_c are the voltage readings for measurements and electrical calibration, respectively, and f is the molar flow rate of the mixture.

The molar flow rate f_i of the ith component flowing into the mixing cell is obtained from the formula

$$f_i = \rho_i V_i / M_i \tag{2}$$

where ρ_i and M_i are the density and molar mass, respectively, and V_i is the volumetric flow rate of component i. Experimental data of excess molar enthalpies, H^E_m, are shown in Table 2 and represented in Figure 1. The uncertainty of H^E_m values is of the order 1%.

The heat capacity measurements were performed using a Perkin-Elmer DSC-7 differential scanning calorimeter, equipped with a model PII intracooler.

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 for all three scans, sample, blank, and standard, similar initial and final isotherm levels were reached. 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 %.

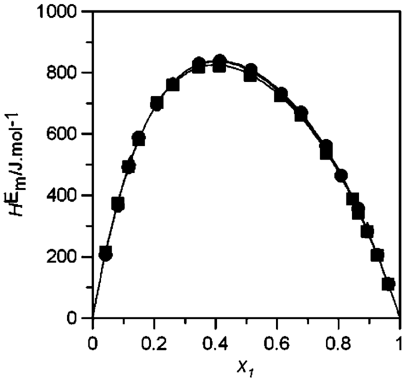

Figure 1. Excess molar enthalpies, H^E_m, for the binary mixtures DMSO (1) + 1-propanol (2). ■, ●, and ▲ refer to (288.15, 298.15, and 308.15) K, respectively. Full line, eq 11.

Table 3. Experimental Liquid Heat Capacities of 1-Propanol at Atmospheric Pressure

	C_p		C_p		C_p
T/K	J·mol^{-1}·K^{-1}	t/K	J·mol^{-1}·K^{-1}	T/K	J·mol^{-1}·K^{-1}
288.15	139	308.15	151.0	323.15	160.1
293.15	142.3	313.15	153.7	328.15	164.5
298.15	144.9	318.15	157.1	333.15	167.8
303.15	148.2				

Table 4. Adjustable Parameters of Equation 3 and Standard Deviation for 1-Propanol

			$\sigma(C_p)$
c_0	c_1	c_2	J·mol^{-1}·K^{-1}
171.54	−0.7535	0.0022	0.4

The experimental molar heat capacities, C_p, of 1-propanol (from 288.15 to 333.15) K at normal pressure are listed in Table 3 and represented in Figure 2. Values of C_p referring to DMSO were reported in a previous paper.[3] The expression used to fit the C_p values is

$$C_p = c_o + c_1(T/\mathrm{K}) + c_2(T/\mathrm{K})^2 \tag{3}$$

and C^E_p values were calculated by

$$C^E_p = C_p - x_1 C_{p1} - x_2 C_{p2} \tag{4}$$

where C_{pi} are the molar heat capacities of pure compounds.

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

The uncertainties of C_p are estimated to be less than 1 %, which leads to an uncertainty of the excess molar heat capacities, C^E_p of ±1 J·mol^{-1}·K^{-1}. Values of C_p and C^E_p of the mixtures are reported in Table 5.

Table 5. Experimental Liquid Heat Capacities, C_p, and Excess Heat Capacities, C_p^E, of DMSO + 1-Propanol at (288.15, 298.15, and 308.15) K

	C_p	C_p^E		C_p	C_p^E		C_p	C_p^E
x_1	$J \cdot mol^{-1} \cdot K^{-1}$	$J \cdot mol^{-1} \cdot K^{-1}$	x_1	$J \cdot mol^{-1} \cdot K^{-1}$	$J \cdot mol^{-1} \cdot K^{-1}$	x_1	$J \cdot mol^{-1} \cdot K^{-1}$	$J \cdot mol^{-1} \cdot K^{-1}$
				T/K = 288.15				
0.0514	138.1	−1.3	0.418	135.3	−6.9	0.7975	140.0	−5.2
0.1127	137.3	−2.6	0.5029	135.7	−7.2	0.8537	141.7	−4.0
0.2114	136.2	−4.5	0.6216	136.7	−7.1	0.8994	143.1	−2.9
0.3163	135.5	−6.0	0.7068	138.1	−6.4	0.9429	144.6	−1.8
				T/K = 298.15				
0.0514	143.6	−1.7	0.4180	138.6	−9.4	0.7975	143.5	−7.4
0.1127	142.3	−3.4	0.5029	138.6	−10.0	0.8537	145.4	−5.9
0.2114	140.3	−6.1	0.6216	139.7	−9.9	0.8994	147.4	−4.3
0.3163	139.1	−8.2	0.7068	141.1	−9.1	0.9429	149.4	−2.6
				T/K = 308.15				
0.0514	149.7	−1.7	0.4180	141.4	−11.2	0.7975	144.7	−9.2
0.1127	147.9	−3.7	0.5029	140.9	−12.0	0.8537	146.8	−7.3
0.2114	145.2	−6.7	0.6216	141.2	−12.1	0.8994	148.7	−5.6
0.3163	143.0	−9.3	0.7068	142.4	−11.2	0.9429	151.0	−3.4

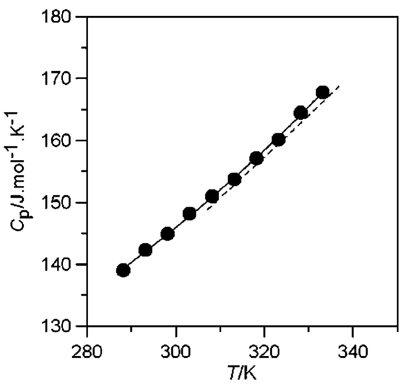

Figure 2. Heat capacities of 1-propanol in the range (288.15−333.15) K. Full line, eq 3, dashed line, comparison with literature data.[29]

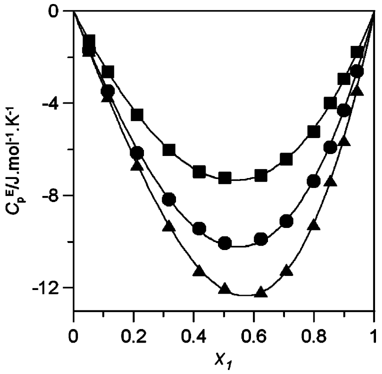

Figure 3. Excess molar heat capacities, C_p^E, for the binary mixtures DMSO (1) + 1-propanol (2). ■, ●, and ▲ refer to (288.15, 298.15, and 308.15) K, respectively. Full line, eq 11.

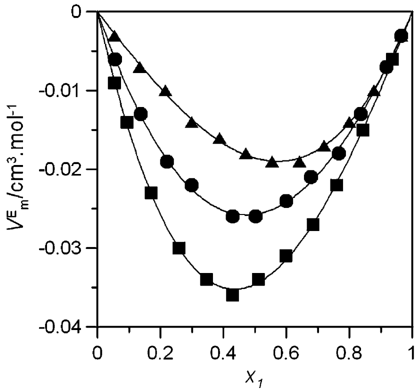

Figure 4. Excess molar volumes, V^E_m, for the binary mixtures DMSO (1) + 1-propanol (2). ■, ●, and ▲ refer to (288.15, 298.15, and 308.15) K, respectively. Full line, eq 11.

Density Measurements. Liquid mixtures were prepared by mass using a Mettler balance with an uncertainty of ± 0.0001 g. The uncertainty of the mole fraction, x_1, of DMSO was estimated to be less than $\pm 2 \cdot 10^{-4}$. To prevent the samples from preferential evaporation, the mixtures were prepared by transferring aliquots via syringe into suitably stoppered bottles.

Excess molar volumes, V^E_m, reproducible to ± 0.003 $cm^3 \cdot mol^{-1}$, 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).[25]

All measurements have been determined at a constant temperature using an external ultra-thermostat bath circulator (Heto, type 01 DTB 623, Birkeròd, Denmark), precision ± 0.005 K, and temperatures have been detected by a digital thermometer (Anton Paar, type CTK 100).

Before each series of measurements, the apparatus was calibrated at atmospheric pressure using double-distilled water and dry air, whose densities were taken from literature.[26,27] The uncertainty in density was $\pm 1.5 \cdot 10^{-5}$ $g \cdot cm^{-3}$ at a temperature of 308.15 K. Correspondingly, the uncertainty in V^E_m is estimated as ± 1 %. Before the measurements, the apparatus has been checked by determining V^E_m using the test mixture[28] at 298.15 K. Our results agree with those of literature with a discrepancy of ± 0.5 % in the central range of mole fraction of benzene.

The excess molar volumes, V^E_m, were computed by the following equation

$$V^E_m = (x_1 M_1 + x_2 M_2)/\rho - x_1 M_1/\rho_1 - x_2 M_2/\rho_2 \qquad (5)$$

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

Viscosity Measurements. The kinematic viscosities,ν, 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 (0.53 and 0.63) mm and were used for kinematic ranges of (0.8 to 1.2) $mm^2 \cdot s^{-1}$, 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

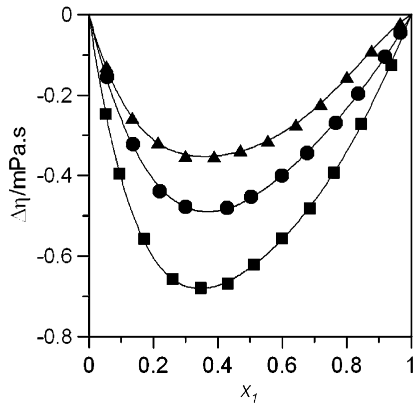

Figure 5. Experimental deviation in viscosities, $\Delta\eta$, for the binary mixtures DMSO (1) + 1-propanol (2). ■, ●, and ▲ refer to (288.15, 298.15, and 308.15) K, respectively. Full line, eq 11.

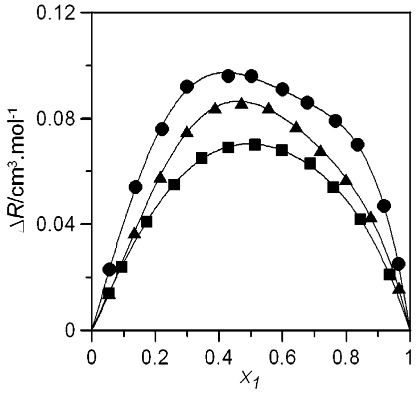

Figure 6. Deviation in refractive indices, ΔR, for the binary mixtures DMSO (1) + 1-propanol (2). ■, ●, and ▲ refer to (288.15, 298.15, and 308.15) K, respectively. Full line, eq 11.

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

$$\nu = \eta/\rho = k(t - \theta) \tag{6}$$

where η is the absolute (dynamic) viscosity, ρ is the density, t is the flow time, θ is the kinetic energy correction, and k is the viscometer constant, determined by calibration. In the whole set of experiments, flow times were maintained >200 s, by selecting viscosimeters with appropriate values of k.

Equation 6 and the values of ρ allow for calculation of the deviation in viscosity, $\Delta\eta$, from the definition

$$\Delta\eta = \eta - \omega_1\eta_1 - \omega_2\eta_2 \tag{7}$$

where η_k is the viscosity of the pure component k and ω_k is its mass fractions in the mixture.

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 less than ± 0.0001 units. A minimum of three independent readings were 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.

Table 6. Densities, ρ, Excess Molar Volumes, V_m^E, Dynamic Viscosities, η, Deviations in Dynamic Viscosities, $\Delta\eta$, Refracive Indices, n_D, and Deviations in Refractivity, ΔR, for Binary Mixtures Containing DMSO + 1-Propanol at (288.15, 298.15, and 308.15) K

x_1	ρ $g\cdot cm^{-3}$	V_m^E $cm^3\cdot mol^{-1}$	η mPa·s	$\Delta\eta$ mPa·s	n_D	ΔR $cm^3\cdot mol^{-1}$
			T/K = 288.15			
0.0533	0.82273	−0.009	2.251	−0.246	1.3942	0.014
0.0938	0.83433	−0.014	2.100	−0.396	1.3979	0.024
0.1708	0.85651	−0.023	1.937	−0.557	1.4050	0.041
0.2592	0.88215	−0.030	1.835	−0.657	1.4132	0.055
0.3460	0.90754	−0.034	1.810	−0.679	1.4212	0.065
0.4294	0.93212	−0.036	1.819	−0.668	1.4290	0.069
0.5115	0.95649	−0.034	1.864	−0.621	1.4367	0.070
0.5981	0.98238	−0.031	1.927	−0.556	1.4449	0.068
0.6853	1.00866	−0.027	1.999	−0.482	1.4532	0.063
0.7596	1.03123	−0.022	2.086	−0.393	1.4603	0.054
0.8438	1.05701	−0.015	2.206	−0.271	1.4685	0.042
0.9368	1.08571	−0.006	2.348	−0.126	1.4774	0.021
			T/K = 298.15			
0.0554	0.81518	−0.006	1.799	−0.155	1.3889	0.023
0.1366	0.83830	−0.013	1.635	−0.322	1.3966	0.054
0.2200	0.86221	−0.019	1.522	−0.438	1.4045	0.076
0.2987	0.88495	−0.022	1.486	−0.477	1.4119	0.092
0.4289	0.92294	−0.026	1.487	−0.481	1.4239	0.096
0.5022	0.94455	−0.026	1.517	−0.452	1.4307	0.096
0.5992	0.97337	−0.024	1.575	−0.399	1.4398	0.091
0.6770	0.99669	−0.021	1.633	−0.344	1.4472	0.086
0.7656	1.02343	−0.018	1.710	−0.269	1.4558	0.079
0.8358	1.04481	−0.013	1.786	−0.196	1.4627	0.070
0.9181	1.07004	−0.007	1.881	−0.104	1.4705	0.047
0.9646	1.08438	−0.003	1.942	−0.045	1.4747	0.025
			T/K = 308.15			
0.0537	0.80644	−0.003	1.439	−0.129	1.3843	0.014
0.1336	0.82896	−0.007	1.319	−0.256	1.3916	0.037
0.2147	0.85203	−0.010	1.264	−0.317	1.3991	0.058
0.2987	0.87611	−0.014	1.237	−0.351	1.4070	0.075
0.3876	0.90181	−0.016	1.243	−0.352	1.4152	0.084
0.4707	0.92608	−0.018	1.265	−0.337	1.4229	0.086
0.5552	0.95093	−0.019	1.296	−0.313	1.4308	0.084
0.6418	0.97665	−0.019	1.343	−0.273	1.4389	0.077
0.7191	0.99978	−0.017	1.401	−0.221	1.4462	0.068
0.7998	1.02411	−0.014	1.474	−0.155	1.4540	0.057
0.8770	1.04758	−0.010	1.545	−0.089	1.4614	0.043
0.9650	1.07453	−0.003	1.621	−0.021	1.4698	0.016

The sample mixtures were directly injected into the prism assembly of the instrument using an airtight hypodermic syringe, 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, ΔR, were calculated from the Lorentz−Lorenz equation

$$\Delta R = R_m - \sum_{i=1}^{2} R_i\varphi_\iota \tag{8}$$

where R_i and R_m are the molar refraction of pure components and of mixture, respectively, and φ_i is the volume fraction of the ith component, given as

$$\varphi_i = x_i V_i / \sum_{i=1}^{2} x_i V_i \tag{9}$$

where $V_i = M_i/\rho_i$. The molar refraction, R_i, was obtained from the formula (Lorentz−Lorenz)

$$R_i = \{[n^2_{D(i)} - 1]/[n^2_{D(i)} + 2]\}\cdot V_i \tag{10}$$

where $n_{D(i)}$ is the refractive index for the pure ith component.

Table 7. Adjustable Parameters, a_k, from Equation 11, and Standard Deviations σ (Q), Equation 12, of DMSO + 1-Propanol at (288.15, 298.15, and 308.15) K

function	a_0	a_1	a_2	a_3	σ(Q)
		T/K = 288.15			
H_m^E/J·mol^{-1}	3201.5	−924.0	1155.5	−460.8	3.5
C_p^E/J·mol^{-1}·K^{-1}	−29.189	−4.148			0.047
V_m^E/cm^3·mol^{-1}	−0.1390	0.0406			0.0003
$\Delta\eta$/mPa·s	−2.5155	1.1740	−1.2041	0.5586	0.005
ΔR/cm^3·mol^{-1}	0.2815	−0.0046	0.0429	0.0517	0.0005
		T/K = 298.15			
H_m^E/J·mol^{-1}	3266.8	−903.0	1064.1	−379.3	5.2
C_p^E/J·mol^{-1}·K^{-1}	−40.469	−7.972			0.093
V_m^E/cm^3·mol^{-1}	−0.1031	0.0113			0.0002
$\Delta\eta$/mPa·s	−1.8269	0.9245	−0.5033	−0.0093	0.004
ΔR/cm^3·mol^{-1}	0.3826	−0.0792	0.2198	0.2667	0.0007
		T/K = 308.15			
H_m^E/J·mol^{-1}	3251.7	−953.1	1058.3	−321.9	5.3
C_p^E/J·mol^{-1}·K^{-1}	−48.268	−14.799			0.075
V_m^E/cm^3·mol^{-1}	−0.0743	−0.0232			0.00005
$\Delta\eta$/mPa·s	−1.3283	0.5798	−0.3649	0.6278	0.002
ΔR/cm^3·mol^{-1}	0.3437	−0.0589	0.0192	0.2017	0.00003

Table 6 collects densities, ρ, excess molar volumes, V_m^E, viscosities, η, deviations in viscosities, $\Delta\eta$, refractive indices, n_D, and deviations in refractive indices, ΔR.

The variation of $H_m{}^E$, $C_p{}^E$, $V_m{}^E$, $\Delta\eta$, and ΔR with composition are expressed by the Redlich−Kister polynomial

$$Q = x_1x_2 \sum_{k\geq 0} a_k(x_1 - x_2)^k \tag{11}$$

where Q refers to H_m^E, C_p^E, V_m^E, $\Delta\eta$, and ΔR.

The adjustable parameters, a_k, were determined by a least-squares method, fitting the experimental values to eq 11, and the results are given in Table 7. The standard deviations, $\sigma(Q)$, reported in Table 7 were defined as

$$\sigma(Q) = |\phi_{\min}/(N - n)|^{0.5} \tag{12}$$

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

$$\phi = \sum_{k=1}^{N} \eta_k{}^2 \tag{13}$$

where $\eta_k = Q_{\text{calcd}} - Q$. Q is the experimental value and Q_{calcd} is evaluated through eq 11.

Results and Discussion

Comparison of the H_m^E, C_p, C_p^E, V_m^E, $\Delta\eta$, and ΔR curves in Figures 1−6 shows that H_m^E values are independent of temperature while a strong temperature dependence is observed for other properties.

Particularly, V_m^E and $\Delta\eta$ are both negative and have the same trend as a function of temperature, that is, an increase with increasing temperature. Instead, C_p^E values show a decrease with increasing temperature, while ΔR values have no monotone trend.

Positive values of H_m^E are compatible with the presence of 1-propanol in the mixtures, since breaking of the strong hydrogen bonds of alcohol implies high energy intake, which is not compensated by the interactions between the S═O and OH groups of DMSO and alcohol, respectively, after mixing. The consequent reduction of average molecular size is in turn consistent with the volume and viscosity decrease, as can be seen from Figures 4 and 5.

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**, in press.

(4) 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.

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

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

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

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

(9) Kimura, T.; Tomoko, M.; Takayuki, C.; Sadao, T. Thermodynamics of Liquid Mixtures Containing Methyl Methylthiomethyl Sulfoxide. VI. Excess Enthalpies of (Methyl Methylthiomethyl sulfoxide + Methanol, Ethanol, or 1-Propanhol) and (Dimethyl Sulfoxide + Methanol, + Ethanol, or + 1- Propanol) at 298.15 K. *Netsu Sokutei* **1990**, *17(2)*, 67−72.

(10) Kimura, T.; Takanori, M.; Tadashi, K. Enthalpies of Solution of Aliphatic Compounds in Dimethyl Sulfoxide. *Thermochim. Acta* **2004**, *416* (1−2), 129−134.

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

(12) Nikam, P. S.; Jadhav, M. C.; Hasan, M. Volumetric, Viscometric and Ultrasonic Behaviour of Dimethyl Sulfoxide with Normal Alcohols ($C_1 - C_4$) at 308.15K. *J. Mol. Liq.* **1998**, *76*, 1−11.

(13) Barthel, J.; Gores, H.-J.; Kraml, L. Effects of Electronegative Substituents of Anions on Ion-Pair Formation. 1. Temperature Dependence of the Conductivity of Lithium Fluoroacetate and Alkali-Metal Acetate Solutions in Dimethyl Sulfoxide. *J. Chem Phys.* **1996**, *4*, 1283−1287.

(14) Ritzoulis, G.; Excess Properties of Binary Liquid Systems Dimethyl Sulfoxide + 2-Propanol and Propylene Carbonate + 2-Propanol. *Can. J. Chem.* **1989**, *67*, 1105−1108.

(15) Chauhan, M. S.; Sharma, K. C.; Gupta, S.; Chauhan, S.; Syal, V. K. Conductance and Viscosimetric Studies of Some Tetraalkylammonium and Sodium Salts in Acetonitrile-dimethyl Sulfoxide Mixtures at 35 DEGC. *Collect. Czech. Chem. Commun.* **1992**, *10*, 2078−2088.

(16) Blaszczak, Z.; Farhoud, M. Optical Kerr Effect in a Series of *n*-Alcohols. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 2455−2458.

(17) Rodriguez, A.; Canosa, J.; Tojo, J. Physical Properties of Binary Mixtures of (*tert*-Butyl Mrthyl Ether + alcohols) from T = 288.15 K to T = 298 K. *J. Chem. Thermodyn.* **1999**, *31*, 1009−1024.

(18) Pal, A.; Kumar, H. Temperature Dependence of the Volumetric Properties of Some Alkoxypropanols + *n*-Alkanols Mixtures. *J. Chem. Thermodyn.* **2004**, *36*, 173−182.

(19) Rattan, V. K.; Sukhemehar, S.; Sethi, B. P. S. Viscosities, Densities, and Ultrasonic Velocities of Binary Mixtures of Ethylbenzene with Ethanol, 1-Propanol, and 1-Butanol at (298.15 and 308.15) K. *J. Chem. Eng. Data* **2004**, *49*, 1074−1077.

(20) Shinomija, T. Dielecric Dispersion and Intermolecular Association for 28 Pure Liquid Alcohols. The Position Dependence of Hydroxyl Group in the Hydrocarbon Chain. *Bull. Chem. Soc. Jpn.* **1989**, *3*, 908−914.

(21) Francesconi, R.; Comelli, F. Liquid-Phase Enthalpy of Mixing for the System 1,3-Dioxolane-Chlorobenzene in the Range 288.15−313.15 K. *J. Chem. Eng. Data* **1986**, *31*, 250−253.

(22) Monk, P.; Wadsö, I. A Flow Micro Reaction Calorimeter. *Acta Chem. Scand.* **1968**, *22*, 1842−1852.
(23) Gmehling, I. Excess Enthalpies for 1,1,1-Trichloroethane with Alkanes, Ketones, and Esters. *J. Chem. Eng. Data* **1993**, *38*, 143−146.
(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 Praktishen Temperaturskala von 1968. *PTB-Mitt.* **1971**, *6/71*, 412.
(28) Wilhelm, E. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1985**, 164.
(29) Becker, L.; Aufderhaar, O.; Gmehling, J. Measurement of Heat Capacities for Nine Organic Substances by Tian-Calvet Calorimetry. *J. Chem. Eng. Data* **2000**, *45*, 661−664.

Received for review April 6, 2006. Accepted June 12, 2006.

JE0601513