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Excess Enthalpies, Heat Capacities, Densities, Viscosities and Refractive Indices of Dimethyl Sulfoxide + Three Aryl Alcohols at 308.15 K and Atmospheric Pressure

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Enthalpies of mixing, heat capacities, densities, viscosities, and refractive indices of dimethyl sulfoxide + benzyl alcohol, + 2-phenylethanol, and + 3-phenyl-1-propanol have been measured at 308.15 K and at atmospheric pressure using an LKB micro-calorimeter, a Perkin-Elmer differential scanning calorimeter, an Anton Paar density meter, a Schott-Geräte AVS unit, and an Abbe refractometer, respectively. Heat capacities were determined at (298.15, 308.15, and 318.15) K. The results were fitted to the Redlich−Kister polynomial equation to derive the adjustable parameters and standard deviations and were used to study the nature of the molecular interactions in these mixtures.

Introduction

Dimethyl sulfoxide (DMSO) was chosen in this study because of its wide range of applicability as a solvent in chemical and biological processes, involving both plants and animals. Furthermore, DMSO is widely used in pharmaceutical applications, enzyme-catalyzed reactions, veterinary medicine, dermatology, experimental immunology, and microbiology.[1] The main pharmacological use of DMSO is as a vehicle for drugs such as idoxuridine: it aids penetration of the drug into the skin, possibly enhancing the drugs effect. Further reported activities of DMSO include membrane penetration, anti-inflammatory effects, local analgesia, weak bacteriostasis, diuresis, vasodilatation, dissolution of collagen, and free-radical scavenging.[2] In veterinary medicine, it is used in therapy category, in treatment of interstitial cystitis and scleroderma, and topically to reduce swelling due to trauma.[3]

DMSO is also a solvent for many organic compounds including fats, carbohydrates, dyes, resins, and polymers. It is employed as antifreeze of hydraulic fluid when mixed with water, for cryopreservation and storing of cultured cells. DMSO exhibits strong self-association, it is a highly polar aprotic solvent because of its S=O group, and it has a large dipole moment and relative permittivity, showing values of $\mu = 4.06$ D and $\epsilon = 46.45$ at 298.15 K.

This paper reports experimental excess molar enthalpies (H_m^E), heat capacities (C_p), densities (ρ), dynamic viscosities (η), and refractive indices (n_D) for binary mixtures containing DMSO + three aryl alcohols, namely, benzyl alcohol, 2-phenylethanol, and 3-phenyl-1-propanol. Although these three aryl alcohols have small values of permittivity and dipole moment (for example, benzyl alcohol has values of $\mu = 1.66$ D and $\epsilon = 11.916$ at 313.15 K), they are self-associated through hydrogen bonding. Therefore, thermodynamic properties of DMSO + these aryl alcohols are of interest because DMSO provides an S=O group and alcohols provide an OH group for interactions.

This paper aims to determine the thermophysical properties of these mixtures in order to investigate the influence of increasing chain length in the aryl alcohols and to obtain further insight into the interactions between molecules.

Experimental values were correlated using the Redlich−Kister polynomial with adjustable parameters, and the standard deviation between experimental and calculated values are reported in Table 4. To our knowledge, the experimental data reported in this paper are not available in the literature.

Experimental Section

Materials. DMSO, analytical grade 99.9 %, was purchased from Aldrich; benzyl alcohol, purity 99.8 %, was from Riedel-de-Haën; while 2-phenylethanol and 3-phenyl-1-propanol, both purities >99 %, were from Fluka. All liquids were used without further purification.

Before use, the components were degassed ultrasonically (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 gas-chromatograph model 5890 supplied by an HP (cross-linked 5 % ME siloxane) capillary column, and the obtained values were complied with purchaser specifications. Experimental values of densities, viscosities, and refractive indices for the pure components were compared with literature data[4−10] as shown in Table 1.

Calorimetric Measurements. A flow microcalorimeter (LKB, model 2107, Producer AB, Bromma, Sweden), thermostated at (308.15 ± 0.01) K, was used to measure the excess molar enthalpies (H_m^E). The apparatus consists of a flow-mixing cell, a reference cell, a thermostatic water bath, a data acquisition unit, and two automatic burets (ABU, Radiometer, Copenhagen, Denmark) necessary to pump the pure liquids into the mixing cell of the calorimeter. The temperature of the bath was controlled within ± 0.01 K. The calibration of the apparatus and its operating procedure are described elsewhere.[11,12] The performance and reliability of the microcalorimeter were checked by the test

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

		ρ/g·cm^{-3}		η/mPa·s		n_D	
component	T/K	this paper	lit.	this paper	lit.	this paper	lit.
DMSO	298.15	1.09568	1.09569[a]	1.989	1991[b]	1.4775	1.47754[b]
	308.15	1.08531	1.08548[c]	1.645	1.654[b]	1.4730	1.4729[d]
	308.15				1.614[c]		
benzyl alcohol	298.15	1.04165	1.0416[e]	5.211		1.5377	1.5378[e]
	308.15	1.03366	1.0329[f]	4.125		1.5350	
2-phenylethanol	308.15	1.00879	1.00915[g]	7.438		1.5267	
3-phenyl-1-propanol	308.15	0.99117		10.126		1.521	

[a] Ref 5. [b] Ref 4. [c] Ref 6. [d] Ref 7. [e] Ref 8. [f] Ref 9. [g] Ref 10.

mixtures hexane + cyclohexane, benzene + cyclohexane, and methanol + water. The experimental values of H_m^E agreed with literature data[13] within 1 %. Miscibility of the components was tested prior to measurements, and components were found to be completely miscible over the whole concentration range. Mole fractions of mixtures were computed from densities; volumetric flow rates of components, selected to cover the entire mass fraction range, were stated by the automatic burets. The total flow rates were usually kept at about 0.4 cm^3·min^{-1}, but in the dilute region, the total flow rates may increase up to 0.8 cm^3·min^{-1}. The experimental uncertainties in H^E were estimated to be less than 0.5 % over the most of the composition range.

The H_m^E values were computed from the following relationship:

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

where I and R are the electrical current and resistance in the 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 H_m^E are reported in Table 2.

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 scanning rate of 5 K·min^{-1} the sample run, the blank run, and the standard sample (sapphire) run.[14] 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 error for repeated data is less than 0.1 %.

The experimental C_p data of the mixtures are reported in Table 3. Figure 1 displays, as an example, the graph of the data obtained at 308.15 K. The expression used to fit the heat capacities C_p is

$$C_p/\text{J·mol}^{-1}\text{·K}^{-1} = c_o + c_1x_1 + c_2{x_1}^2 \tag{3}$$

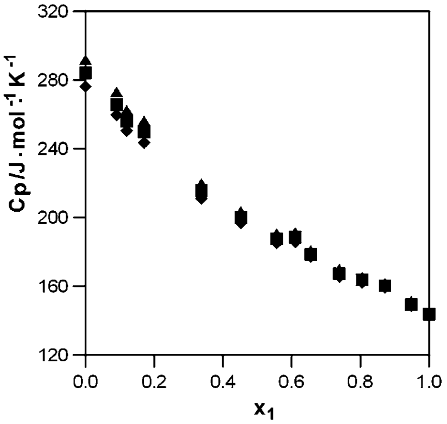

Figure 1. Experimental liquid heat capacities of DMSO (1) + 3-phenyl-1-propanol (2). ◆, ■, and ▲ refer to mixtures at (298.15, 308.15, and 318.15) K, respectively.

Table 2. Excess Molar Enthalpies (H_m^E) for Binary Mixtures Containing DMSO + Three Aryl Alcohols at 308.15 K

x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}
DMSO (1) + Benzyl Alcohol (2)					
0.0571	−476	0.4209	−1499	0.8532	−495
0.1080	−811	0.4920	−1424	0.8971	−345
0.1537	−1040	0.5924	−1272	0.9208	−257
0.1950	−1217	0.6856	−1033	0.9457	−164
0.2666	−1390	0.7440	−841	0.9721	−88
0.3264	−1497	0.8135	−613		
DMSO (1) + 2-Phenylethyanol (2)					
0.0655	−389	0.4569	−929	0.8707	−269
0.1230	−628	0.5286	−867	0.9099	−192
0.1738	−776	0.6273	−732	0.9309	−147
0.2190	−867	0.7163	−572	0.9528	−98
0.2961	−946	0.7709	−468	0.9759	−50
0.3593	−975	0.8347	−345		
DMSO (1) + 3-Phenyl-1-propanol (2)					
0.0737	−227	0.4885	−333	0.8843	7
0.1373	−344	0.5600	−270	0.9162	14
0.1927	−398	0.6563	−177	0.9386	18
0.2414	−429	0.7413	−90	0.9582	17
0.3232	−422	0.7925	−48	0.9787	11
0.3890	−396	0.8514	−13		

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 accuracy of the excess molar heat capacities (C_p^E) of ± 1 J·mol^{-1}·K^{-1}. C_p^E values were evaluated by the formula:

$$C_p^E/\text{J·mol}^{-1}\text{·K}^{-1} = C_p - x_1C_{p1} - (1 - x_1)C_{p2} \tag{4}$$

where C_{p1} and C_{p2} are the heat capacities of pure compo-

Table 3. Heat Capacities of Mixtures (C_p) for DMSO + Benzyl Alcohol (BA), + 2-Phenylethanol (PE), and + 3-Phenyl-1-propanol (PP) at (298.15, 308.15, and 318.15) K

x_1	C_p/J·mol^{-1}·K^{-1}		
	298.15 K	308.15 K	318.15 K
DMSO (1) + Benzyl Alcohol (2)			
0.0000	200.4	203.9	207.2
0.087064	196.4	201.5	206.4
0.143896	189.3	193.7	198.6
0.270827	168.3	172.9	177.0
0.381711	167.0	170.3	174.1
0.496372	162.3	164.4	166.7
0.542236	160.1	162.4	164.9
0.596621	159.3	161.5	163.6
0.686320	146.6	149.1	150.8
0.771089	146.9	148.1	149.8
0.857671	149.7	151.2	152.5
0.923696	149.0	150.2	151.4
0.950779	146.4	147.6	148.8
1.0000	142.7	143.5	144.6
DMSO (1) + 2-Phenylethanol (2)			
0.0000	239.6	245.3	251.6
0.085810	235.0	240.8	246.5
0.163767	218.3	223.2	228.7
0.299943	190.7	194.2	198.1
0.420494	185.0	188.4	191.3
0.518991	185.5	188.2	190.7
0.629341	169.3	171.3	173.6
0.671277	171.0	172.8	174.9
0.706559	162.6	164.6	166.5
0.791908	162.7	164.8	166.8
0.859577	156.2	157.3	159.1
0.937011	157.8	159.6	160.0
0.968842	143.5	144.8	145.9
1.0000	142.7	143.5	144.6
DMSO (1) + 3-Phenyl-1-propanol (2)			
0.0000	276.3	284.1	291.8
0.090500	259.9	265.7	273.0
0.120398	250.3	256.0	262.8
0.171194	243.4	249.7	256.2
0.337513	211.1	215.5	220.0
0.451990	196.9	200.0	203.5
0.557097	185.1	187.5	190.7
0.610081	185.8	188.7	191.4
0.656700	177.0	178.3	180.9
0.739632	165.6	167.2	170.0
0.805986	162.2	163.9	165.4
0.871844	159.2	160.5	161.9
0.948660	148.5	149.3	151.3
1.0000	142.7	143.5	144.6

Table 4. Adjustable Parameters (c_k) of the Heat Capacity Correlation (Eq 3), and Standard Deviations ($\sigma(C_p)$) for DMSO + Benzyl Alcohol (BA) + 2-Phenylethanol (PE) and + 3-Phenyl-1-propanol (PP) at (298.15, 308.15, and 318.15) K

mixture	T/K	c_0	c_1	c_2	$\sigma(C_p)$/J·mol^{-1}·K^{-1}
DMSO + BA	298.15	201.9	−110.7	54.6	3.8
	308.15	206.5	−114.3	54.3	3.7
	318.15	211.1	−117.3	53.6	3.8
DMSO + PE	298.15	240.2	−142.8	50.4	5.8
	308.15	246.2	−150.6	53.4	6.0
	318.15	252.6	−159.5	56.9	6.0
DMSO + PP	298.15	274.8	−196.4	60.1	3.3
	308.15	282.2	−207.8	72.8	3.4
	318.15	290.2	−219.3	77.6	3.4

nents. The C_p^E values at 308.15 K of the DMSO (1) + 3-phenyl-1-propanol (2) mixtures are shown in Figure 2. The data obtained for the same mixtures at (298.15 and 318.15) K exhibit similar trends, whereas those containing benzyl alcohol and 2-phenylethanol show somewhat more scatter.

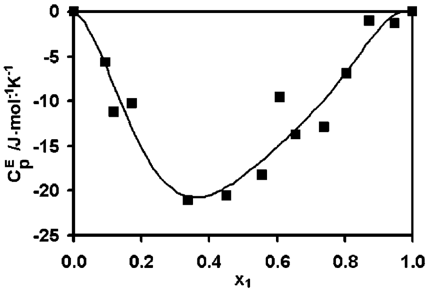

Figure 2. Experimental excess molar heat capacities for binary mixtures containing DMSO (1) + 3-phenyl-1-propanol (2) at 308.15 K. Full line, eq 4.

Density Measurements. Excess molar volumes (V_m^E) reproducible to ± 0.003 cm^3·mol^{-1} have been determined from density measurements with the help of a digital density meter (Anton Paar, model DMA 60, Graz, Austria) equipped with a measuring cell (Anton Paar, type 602).[15]

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). Mixtures were prepared by mass, using a digital balance (Mettler, model AE 160, Switzerland) with an accuracy of ± 0.0001 g. All masses were corrected for buoyancy and evaporation of components. All molar quantities have been based on the relative atomic mass table by IUPAC.[16]

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.[17,18] The uncertainty in density was ± 1.5·10^{-5} g·cm^{-3} at 308.15 K. Correspondingly, the uncertainty in V_m^E is estimated ± 1 % Before measurements, the apparatus has been checked by determining V_m^E using the test mixture benzene + cyclohexane at 298.15 K. Our results agree with those of literature[19] showing a discrepancy of ± 0.5 % in the central range of mole fraction of benzene.

The V_m^E were computed by the following equation:

$$V_m^E = (x_1M_1 + x_2M_2)/\rho - x_1M_1/\rho_1 - x_2M_2/\rho_2 \qquad (5)$$

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 several 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 accuracy of ± 0.01 K. Three sets of viscometers with capillary diameters from 0.53 mm up to 0.84 mm were used for kinematic ranges of (0.8 to 3) mm^2·s^{-1}, respectively. The viscometers were filled with 15 cm^3 of solution for each measurement. The calibration of the viscometers 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 determined according to

$$\nu = \eta/\rho = k(t - \theta) \qquad (6)$$

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 viscometers with appropriate values of k.

Equation 6 and the values of ρ allow 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 at the sodium D-line (n_D) were measured using a thermostated Abbe refractometer (Carl Zeiss, model G, Jena, Switzerland) with accuracy less than ± 0.0001 units. 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 double-distilled water, toluene, cyclohexane, and carbon tetrachloride at defined temperatures.[4] 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 308.15 K before the experiments in order to achieve a quick thermal equilibrium. The molar refraction deviations (ΔR) were calculated from the Lorentz−Lorenz equation:

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

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

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

where $V_i = M_i/\rho_i$.

The molar refraction (R_i) was obtained from the formula (Lorentz−Lorenz)

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

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

Table 5 collects excess properties regarding excess molar volumes (V_m^E) deviations in viscosities ($\Delta\eta$) and deviations in refractive indices (ΔR). The variation of H_m^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, V_m^E, $\Delta\eta$, and ΔR.

The adjustable parameters (a_k) were determined by least-squares methods, fitting the experimental values to eq 11, and the results are given in Table 6. The standard deviations, $\sigma(Q)$, reported in Table 6 were defined as

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

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

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

Table 5. Densities (ρ), Excess Molar Volumes (V_m^E), Dynamic Viscosities (η), Deviations in Dynamic Viscosities ($\Delta\eta$), Refracive Indices (n_D), and Deviations in Refractive Indices (ΔR) for Binary Mixtures Containing DMSO + Three Aryl Alcohols at 308.15 K

	ρ	V_m^E	η	$\Delta\eta$		ΔR
x_1	g·cm^{-3}	cm^3·mol^{-1}	mPa·s	mPa·s	n_D	cm^3·mol^{-1}
DMSO (1) + Benzyl Alcohol (2)						
0.0641	1.03717	−0.116	3.957	−0.009	1.5328	−0.240
0.1255	1.04032	−0.194	3.787	−0.027	1.5297	−0.482
0.2283	1.04540	−0.278	3.490	−0.069	1.5252	−0.776
0.3275	1.05005	−0.306	3.201	−0.112	1.5204	−0.983
0.4152	1.05407	−0.298	2.949	−0.146	1.5157	−1.105
0.5117	1.05852	−0.267	2.686	−0.170	1.5099	−1.174
0.5942	1.06241	−0.227	2.477	−0.175	1.5048	−1.156
0.6646	1.06587	−0.188	2.306	−0.171	1.4998	−1.103
0.7406	1.06980	−0.144	2.134	−0.154	1.4946	−0.966
0.8125	1.07374	−0.102	1.988	−0.122	1.4891	−0.786
0.8745	1.07757	−0.064	1.858	−0.088	1.4838	−0.562
0.9388	1.08130	−0.031	1.748	−0.049	1.4785	−0.313
DMSO (1) + 2-Phenylethanol (2)						
0.0435	1.01125	−0.052	7.049	−0.137	1.5257	−0.283
0.1521	1.01745	−0.143	6.133	−0.424	1.5224	−0.939
0.2758	1.02460	−0.177	5.162	−0.678	1.5179	−1.538
0.3564	1.02949	−0.175	6.611	−0.763	1.5145	−1.837
0.4566	1.03591	−0.154	3.976	−0.816	1.5099	−2.083
0.5477	1.042183	−0.123	3.446	−0.819	1.5052	−2.177
0.6247	1.04795	−0.094	3.052	−0.767	1.5008	−2.147
0.7102	1.05495	−0.063	2.652	−0.672	1.4956	−1.971
0.7707	1.06033	−0.042	2.398	−0.575	1.4916	−1.748
0.8346	1.06650	−0.023	2.157	−0.446	1.4870	−1.416
0.8653	1.06964	−0.014	2.056	−0.369	1.4846	−1.219
0.9433	1.078316	−0.001	1.806	−0.168	1.4783	−0.581
DMSO (1) + 3-Phenyl-1-propanol (2)						
0.0936	0.99628	−0.037	8.592	−0.740	1.5188	−0.907
0.1499	0.99945	−0.041	7.792	−1.062	1.5172	−1.406
0.2770	1.00707	−0.019	6.190	−1.587	1.5132	−2.363
0.3915	1.01473	0.019	5.032	−1.774	1.5090	−2.998
0.4564	1.01955	0.040	4.488	−1.767	1.5063	−3.247
0.5780	1.02968	0.079	3.629	−1.595	1.5008	−3.442
0.6526	1.03685	0.092	3.180	−1.412	1.4969	−3.367
0.7233	1.04445	0.098	2.801	−1.190	1.4931	−3.116
0.7879	1.05221	0.093	2.487	−0.958	1.4890	−2.734
0.8512	1.06069	0.082	2.208	−0.699	1.4847	−2.177
0.9027	1.06840	0.063	1.993	−0.477	1.4811	−1.568
0.9543	1.07693	0.035	1.801	−0.232	1.4771	−0.808

Table 6. Adjustable Parameters (a_k) from Equation 11, and Standard Deviations $\sigma(Q)$, Equation 12, of DMSO + Aryl Alcohols at 308.15 K

function	a_0	a_1	a_2	a_3	$\sigma(Q)$
DMSO (1) + Benzyl Alcohol (2)					
H_m^E/J·mol^{-1}	−5714.3	2729.5	−552.3	482.5	9.4
V_m^E/cm^3·mol^{-1}	−1.0867	0.7960	−0.1922		0.0011
$\Delta\eta$/mPa·s	−0.6688	−0.3811	0.2378		0.0013
ΔR/cm^3·mol^{-1}	−4.7057	−0.6630			0.0098
DMSO (1) + 2-Phenyethanol (2)					
H_m^E/J·mol^{-1}	−3571.6	2009.3	−917.5	456.1	4.0
V_m^E/cm^3·mol^{-1}	−0.5624	0.6764	−0.1258		0.0013
$\Delta\eta$/mPa·s	−3.2991	0.1012			0.0058
ΔR/cm^3·mol^{-1}	−8.5861	−2.1384	−0.4403	−0.1455	0.0024
DMSO (1) + 3-Phenyl-1-propanol (2)					
H_m^E/J·mol^{-1}	−1283.4	1665.7	−344.9	595.2	2.7
V_m^E/cm^3·mol^{-1}	0.2222	0.6336	−0.1225	0.1127	0.0009
$\Delta\eta$/mPa·s	−6.9320	2.1216			0.012
ΔR/cm^3·mol^{-1}	−13.430	−4.3141	−1.3411		0.008

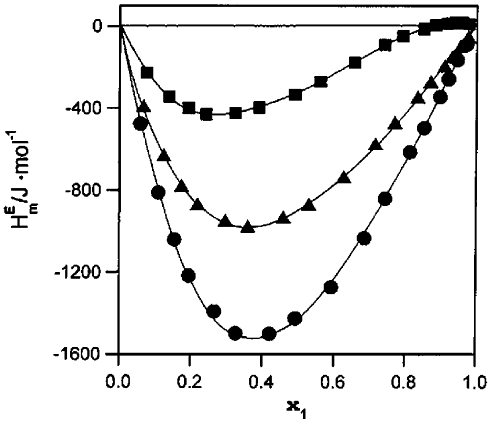

Figure 3. Experimental excess molar enthalpies (H^E_m) for binary mixtures of DMSO (1) + aryl alcohols (2) at 308.15 K. ●, ▲, and ■ refer to mixtures containing benzyl alcohol, 2-phenylethanol, and 3-phenyl-1-propanol, respectively. Full line, Redlich−Kister equation.

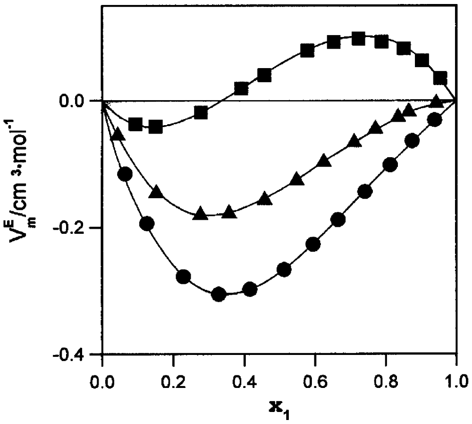

Figure 4. Experimental excess molar enthalpies (V^E_m) for binary mixtures of DMSO (1) + aryl alcohols (2) at 308.15 K. ●, ▲, and ■ refer to mixtures containing benzyl alcohol, 2-phenylethanol, and 3-phenyl-1-propanol, respectively. Full line, Redlich−Kister equation.

where $\eta_k = Q_{\text{calcd}} - Q$. Q is the experimental value, and Q_{calcd} is evaluated through eq 13. Table 6 shows the least-squares analysis of the excess and bulk properties.

Discussion

Experimental values of C_p, C^E_p, H^E_m, V^E_m, $\Delta\eta$, and ΔR of the three DMSO + aryl alcohols mixtures are graphically represented in Figures 1 to 6.

Values of H^E_m are always negative and show a gradual increase with the increase of the number n of CH_2 groups in the side chain of aryl alcohols C_6H_5-$(CH_2)_n$-OH, n varying from 1 to 3. These results may be explained considering that the strength of alcohol decreases with the increase of n[20,21] and that the interaction energy E_{12}, due to hydrogen bonding between molecules of DMSO and alcohol, is the main contribution to $H^E_m \approx E_{11} + E_{22} - 2E_{12}$, owing to the strong interaction between the S=O group of DMSO and the OH group of alcohols.[22]

A different trend was observed in the mixtures containing dimethyl carbonate or diethyl carbonate with the same alcohols.[23] Really, since the interaction energy E_{12} between DMSO and alcohol is strong, H^E_m is negative, whereas E_{22}, the energy due to hydrogen bonding of pure alcohol, prevails in the mixtures containing alkyl carbonates and H^E_m is positive. The mixtures of anisole or phenetole with the same aryl alcohols[24] show very small differences in H^E_m between the curves.

As to the C_p data obtained from differential scanning calorimeter, Figures 2 and 3 report, as an example, values of C_p and C^E_p, respectively, for the mixture DMSO(1) + 3-phenyl-1-propanol(2) as a function of x_1. The mixtures with benzyl alcohol and 2-phenylethanol show similar trends. Table 4 shows the adjustable parameters of the correlation expression (eq 3) together with the standard deviations. The values of C_p decrease with the increase of x_1 and show only a slight temperature dependence.

Values of V^E_m, reported in Table 5 and Figure 4, show the same trend observed for the enthalpy values. In comparison DMSO + benzyl alcohol system shows a sign inversion with composition. The decrease of the interaction energy between dissimilar molecules with the increase of n leads to an increase of the volume after mixing, and thus increasing V^E_m, as a function of n. Therefore, the experimental V^E_m values seem to confirm that interaction energies may be assumed to contribute mainly to the final volume of the system. The n dependence of the deviation in viscosity ($\Delta\eta$, Figure 5) indicates a strong decrease of $\Delta\eta$ with the increasing number of CH_2 groups of alcohol molecule. The curves ΔR versus x_1 show the same trend observed for the excess functions H^E_m, V^E_m, and for $\Delta\eta$, which is a decreasing of ΔR with the increase of molecular size of alcohols.

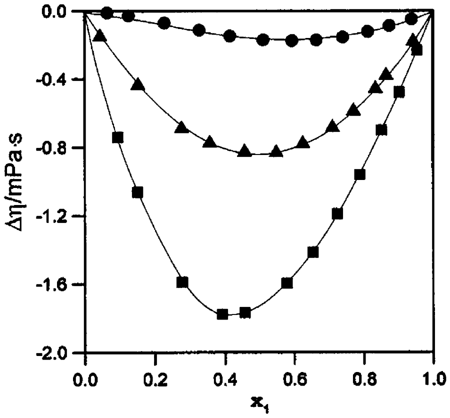

Figure 5. Experimental deviation in viscosities ($\Delta\eta$) for binary mixtures of DMSO (1) + aryl alcohols (2) at 308.15 K. ●, ▲, and ■ refer to mixtures containing benzyl alcohol, 2-phenylethanol, and 3-phenyl-1-propanol, respectively. Full line, Redlich−Kister equation.

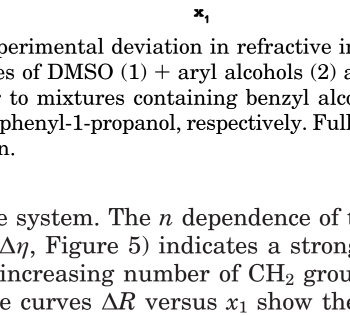

Figure 6. Experimental deviation in refractive indices (ΔR) for binary mixtures of DMSO (1) + aryl alcohols (2) at 308.15 K. ●, ▲, and ■ refer to mixtures containing benzyl alcohol, 2-phenylethanol, and 3-phenyl-1-propanol, respectively. Full line, Redlich−Kister equation.

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