Excess Molar Enthalpies, Molar Heat Capacities, Densities, Viscosities, and Refractive Indices of Dimethyl Sulfoxide + Esters of Carbonic Acid at 308.15 K and Atmospheric Pressure

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Enthalpies of mixing, heat capacities, densities, viscosities, and refractive indices of dimethyl sulfoxide + dimethyl carbonate, + diethyl carbonate, and + propylene carbonate have been measured at 308.15 K and at atmospheric pressure using a 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 pure components were determined in the range $(293.15 < T/\mathrm{K} < 423.15)$. The results were fitted to the Redlich−Kister polynomial equation to derive the adjustable parameters and standard deviations to study the nature of the molecular interactions in the mixtures. Results of excess molar enthalpy were interpreted by an extended modified cell model.

Introduction

The thermophysical, thermodynamic, and bulk properties of binary mixtures are studied for many reasons, the most important of which is to provide information about molecular interactions in the liquid state. We have previously investigated the interactions of dimethyl sulfoxide (DMSO) with glycols and alcohols.[1,2] In this paper, we present new experimental data on excess molar enthalpies $H^{\mathrm{E}}_{\mathrm{m}}$, molar heat capacities $C^{\mathrm{E}}_{\mathrm{p}}$, densities ρ, dynamic viscosities η, and refractive indices n_{D} (for sodium D line) of (DMSO + dimethyl carbonate (DMC)), + diethyl carbonate (DEC), and + propylene carbonate (PC) over the entire range of composition at 308.15 K and at pressure of 0.101325 MPa.

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.[3−5] The thermodynamic study of esters of carbonic acids is arousing an increasing interest owing to their uses in extractions of industrial importance, such as the production of many synthetic and natural resins and polymers,[1,5] in the synthesis of pharmaceuticals,[6] and in agricultural chemistry. Particularly, there is a high interest in the dimethyl carbonate and propylene carbonate applications to storage batteries[7−9] based on intercalation of solutions of carbonates with lithium and bromine in graphite. Such batteries can be recharged thermally at relatively low temperatures. Binary mixtures containing propylene carbonate and other organic solvents, especially aprotic ones, have also great technological and theoretical interest.[10]

The thermodynamic properties of DMSO + esters of carbonic acids depend on the interactions between the S═O group of DMSO and the COOH group of the carbonic acid. Estimations of molecular interactions of binary mixtures and information needed to test existing theories of solutions may be related to the magnitude of excess thermodynamic properties such as excess molar enthalpies $H^{\mathrm{E}}_{\mathrm{m}}$, excess molar heat capacities $C^{\mathrm{E}}_{\mathrm{p}}$, and excess molar volumes $V^{\mathrm{E}}_{\mathrm{m}}$. This paper aims to determine these properties with the purpose to obtain some insight into interactions between molecules and to study the influence on thermodynamic properties of the chain length of the esters of carbonic acids. No data on the binary mixtures studied in this paper have been found in the literature.

Experimental Section

Materials. DMSO and DEC, analytical grade > 99.5 mol % and > 99.6 mol %, were obtained from Fluka, while DMC and PC were Aldrich products showing purities > 99 mol % and 99.7 mol %, respectively, declared from purchaser. 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 GCX model 5890 supplied by a HP (cross-linked 5 % ME siloxane) capillary column, and the obtained values complied with purchaser specifications, within ± 0.01. Experimental values of densities, viscosities, refractive indices, and heat capacities of the pure components were compared with literature data,[11−22] 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, $H^{\mathrm{E}}_{\mathrm{m}}$. 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.[23,24] The performance and reliability of the microcalorimeter were checked by test mixtures.[25] The experimental values of $H^{\mathrm{E}}_{\mathrm{m}}$ agreed with literature data 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

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10.1021/je050444g CCC: $33.50

Table 1. Densities, ρ, Dynamic Viscosities, η, and Refractive Indices, n_D, Heat Capacities, C_p, and Heat of Vaporization, H_v, 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	H_v/K·J·mol^{-1}
DMSO	298.15	1.09532	1.09569[a]	1.989	1.991[b]	1.4775	1.47754[b]	145.4	148.25[a]	52.88[b]
	298.15		1.09529[c]		1.9848[d]					
	308.15	1.08533	1.08548[e]	1.6457	1.654[b]	1.4729	1.4729[f]	148.5		
DMC	298.15	1.06331	1.0632[g]			1.3666	1.3667[h]	157.9		36.7[i]
	308.15	1.05004		2.073		1.0500		161.7		
DEC	298.15	0.96900	0.96904[j]	0.747	0.748[b]	1.3829	1.38287[b]	221.2	220.24[j]	43.6[b]
	308.15	0.95776	0.9579[k]	0.661		1.3780	1.37769[k]	223.4	223.09[j]	
PC	298.15	1.19956	1.1995[l]	2.529	2.530[b]	1.4199	1.4199[b]	174.9		55.2[b]
	308.15	1.18895		2.073		1.4166	1.4163[f]	176.7		

[a] Ref 11. [b] Ref 12. [c] Ref 13. [d] Ref 14. [e] Ref 15. [f] Ref 16. [g] Ref 17. [h] Ref 18. [i] Ref 19. [j] Ref 20. [k] Ref 21. [l] Ref 22.

Table 2. Excess Molar Enthalpies, H_m^E, for Binary Mixtures Containing DMSO + Esters of Carbonic Acid at 308.15 K

x_1	$\frac{H_m^E}{\text{J·mol}^{-1}}$	x_1	$\frac{H_m^E}{\text{J·mol}^{-1}}$	x_1	$\frac{H_m^E}{\text{J·mol}^{-1}}$
		DMSO (1) + DMC (2)			
0.0473	187	0.3735	617	0.8267	406
0.0904	316	0.4427	613	0.8774	322
0.1297	414	0.5438	605	0.9051	264
0.1657	465	0.6414	576	0.9347	190
0.2296	540	0.7045	532	0.9662	103
0.2844	568	0.7815	467		
		DMSO (1) + DEC (2)			
0.0666	377	0.4614	1056	0.8727	523
0.1249	612	0.5330	1042	0.9115	393
0.1764	767	0.6315	969	0.9320	316
0.2221	871	0.7199	860	0.9536	229
0.2999	982	0.7741	748	0.9763	121
0.3635	1033	0.8371	622		
		DMSO (1) + PC (2)			
0.0571	78	0.4209	383	0.8532	253
0.1080	139	0.4920	414	0.8971	197
0.1538	191	0.5924	420	0.9208	158
0.1950	228	0.6857	397	0.9458	110
0.2666	294	0.7441	358	0.9721	58
0.3264	336	0.8135	298		

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 0.0067 cm^3·s^{-1}, but in the dilute region the total flow rates may increase up to 0.013 cm^3·s^{-1}. The experimental uncertainties in H^E were estimated to be less than 0.5 % over 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 excess molar enthalpies, H_m^E, are reported in Table 2 and represented in Figure 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 scanning rate of 5 K·min^{-1}: the sample run, the blank run, and the standard sample (sapphire) run.[26] 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 %.

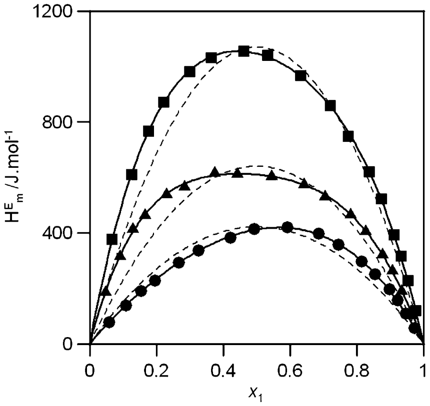

Figure 1. Experimental excess molar enthalpies (H_m^E) for binary mixtures of DMSO (1) + esters of carbonic acid (2) at 308.15 K. ▲, ■, and ● refer to mixtures containing DMC, DEC, and PC, respectively. Full line, eq 11; dashed line, eq 14.

The experimental and calculated heat capacities, C_p, of pure liquids (from 293.15 to 423.15) K at atmospheric pressure are listed in Table 3 and represented in Figure 2.The expression used to fit the heat capacities C_p is

$$C_p = c_0 + c_1(T/\text{K}) + c_2(T/\text{K})^2 \tag{3}$$

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

$$C_p^E = C_p - x_1C_{p1} - (1 - x_1)C_{p2} \tag{4}$$

where C_{p1} and C_{p2} are the heat capacities of pure components.

Density Measurements. Liquid mixtures were prepared by mass using a Mettler balance with an accuracy of ± 0.0001 g. The uncertainty of the mole fraction of DMSO (first component)

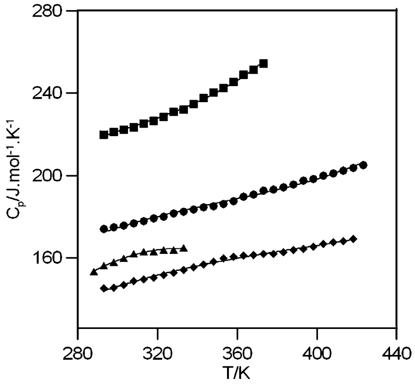

Figure 2. Liquid heat capacities of pure components at 308.15 K. ◆, ■, ▲, and ● refer to DMSO, DMC, DEC, and PC, respectively. Full line, eq 3.

Table 3. Experimental Liquid Heat Capacities of DMSO, DMC, DEC, and PC at Atmospheric Pressure

	C_p/J·mol^{-1}·K^{-1}			
T/K	DMSO	DMC	DEC	PC
288.15		153.2		
293.15	145.0	156.1	219.9	174.1
298.15	145.4	157.9	221.2	174.9
303.15	146.7	159.8	222.3	175.7
308.15	148.5	161.7	223.4	176.7
313.15	149.4	162.9	225.3	177.8
318.15	150.3	163.0	226.6	179.0
323.15	151.5	163.6	228.4	180.0
328.15	152.6	163.8	230.8	181.6
333.15	154.1	164.8	232.0	182.3
338.15	155.3		234.6	183.3
343.15	156.8		237.6	184.5
348.15	158.2		240.3	185.1
353.15	159.6		242.5	186.2
358.15	160.6		245.5	187.4
363.15	160.9		248.9	189.5
368.15	161.3		251.3	190.8
373.15	161.7		254.4	192.7
378.15	161.8			193.0
383.15	162.7			194.3
388.15	163.8			195.6
393.15	164.2			197.3
398.15	165.3			198.2
403.15	166.6			199.9
408.15	167.4			201.0
413.15	168.1			202.3
418.15	169.0			203.6
423.15	172.2			205.1

Table 4. Adjustable Parameters of Equation 3 and Standard Deviation

component	c_0	c_1	c_2	$\sigma(C_p)$/ J·mol^{-1}·K^{-1}
DMSO	30.41	0.5258	−0.0005	0.9
DMC	−504.6	4.0520	−0.0061	0.4
DEC	413.75	−1.5229	0.0029	0.3
PC	173.41	−0.1539	0.0005	0.9

was estimated to be lower than $\pm\ 2 \times 10^{-4}$. To prevent the samples from preferential evaporation, the mixtures were prepared by transferring aliquots via syringe into suitably stoppered bottles.

Excess molar volumes, V_m^E, reproducible to $\pm$ 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).[27]

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). All masses were corrected for buoyancy and evaporation of components. All molar quantities have been based on the relative atomic mass table by IUPAC.[28]

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.[29,30] The uncertainty in density was $\pm\ 1.5 \cdot 10^{-5}$ g·cm^{-3} at a temperature of 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[31] 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_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 0.36 mm up to 0.53 mm were used for kinematic ranges of (0.2 to 0.8) 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 the equation

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

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

$$\Delta\eta = \eta - \omega_1\eta_1 - \omega_2\eta_2 \qquad (7)$$

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. 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.

Table 5. Densities, ρ, Excess Molar Volumes, V_m^E, Dynamic Viscosities, η, Deviations in Dynamic Viscosities, $\Delta\eta$, Refracive Indices, n_D, Deviations in Refractive Indices, ΔR, and Excess Heat Capacities, C_p^E, for Binary Mixtures Containing DMSO + Esters of Carbonic Acid at 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 / $cm^3 \cdot mol^{-1}$	C_p / $J \cdot mol^{-1} \cdot K^{-1}$	C_p^E / $J \cdot mol^{-1} \cdot K^{-1}$
				DMSO (1) + DMC (2)				
0.0596	1.05249	−0.054	0.547	−0.041	1.3682	0.023	160.1	−0.819
0.1027	1.05422	−0.087	0.570	−0.067	1.3725	0.036	158.7	−1.598
0.1913	1.05763	−0.137	0.621	−0.116	1.3814	0.059	156.3	−2.854
0.2791	1.06079	−0.162	0.677	−0.158	1.3903	0.073	153.8	−4.265
0.3710	1.06397	−0.171	0.743	−0.196	1.4000	0.082	151.0	−5.823
0.4598	1.06691	−0.162	0.814	−0.224	1.4092	0.086	148.4	−7.271
0.5007	1.06824	−0.154	0.853	−0.232	1.4136	0.088	147.3	−7.801
0.5479	1.06977	−0.142	0.897	−0.240	1.4188	0.088	146.1	−8.377
0.6260	1.07232	−0.121	0.983	−0.242	1.4276	0.085	144.3	−9.127
0.7427	1.07612	−0.081	1.137	−0.220	1.4411	0.075	143.0	−8.936
0.8572	1.08004	−0.040	1.327	−0.158	1.4550	0.055	143.2	−7.146
0.9283	1.08259	−0.018	1.470	−0.096	1.4638	0.031	145.7	−3.473
				DMSO (1) + DEC (2)				
0.0902	0.96509	−0.072	0.700	−0.050	1.3836	−0.312	216.4	0.735
0.1358	0.96896	−0.101	0.719	−0.076	1.3861	−0.486	213.1	0.795
0.2655	0.98076	−0.159	0.789	−0.133	1.3947	−0.859	203.6	0.884
0.3678	0.99098	−0.183	0.836	−0.169	1.4021	−1.086	196.6	1.402
0.4680	1.00194	−0.188	0.928	−0.194	1.4101	−1.231	189.9	2.098
0.5579	1.01271	−0.179	1.006	−0.204	1.4183	−1.272	183.8	2.663
0.6013	1.01826	−0.171	1.047	−0.206	1.4224	−1.270	180.8	2.826
0.6456	1.02423	−0.161	1.093	−0.204	1.4265	−1.262	177.6	2.906
0.7167	1.03442	−0.140	1.172	−0.195	1.4345	−1.154	172.2	2.752
0.7783	1.04398	−0.117	1.249	−0.178	1.4417	−1.020	167.2	2.312
0.8439	1.05494	−0.084	1.344	−0.148	1.4501	−0.808	161.6	1.538
0.9239	1.06969	−0.043	1.487	−0.084	1.4612	−0.455	154.7	0.576
				DMSO (1) + PC (2)				
0.0506	1.18396	0.061	2.025	−0.026	1.4184	−0.032	174.2	−1.052
0.1139	1.17777	0.130	1.973	−0.051	1.4208	−0.067	171.8	−1.688
0.2014	1.16886	0.213	1.907	−0.080	1.4245	−0.100	169.0	−2.016
0.2976	1.15906	0.286	1.842	−0.104	1.4287	−0.133	166.0	−2.360
0.3820	1.15036	0.332	1.794	−0.116	1.4328	−0.147	163.3	−2.624
0.4759	1.14059	0.362	1.746	−0.123	1.4376	−0.158	160.7	−2.610
0.5376	1.13410	0.370	1.719	−0.124	1.4409	−0.159	159.4	−2.095
0.6343	1.12392	0.357	1.684	−0.118	1.4465	−0.153	158.3	−0.518
0.7176	1.11511	0.322	1.659	−0.107	1.4517	−0.138	158.1	1.626
0.7898	1.10746	0.272	1.645	−0.090	1.4566	−0.114	158.0	3.562
0.8643	10.09957	0.198	1.640	−0.064	1.4620	−0.082	157.1	4.825
0.9376	1.09185	0.103	1.639	−0.033	1.4677	−0.044	154.2	3.928

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):

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

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

Table 5 collects excess properties regarding excess heat capacities C_p^E, excess molar volumes V_m^E, deviations in viscosities $\Delta\eta$, 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:

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

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

The adjustable parameters, a_k, were determined by a least-squares method, fitting the experimental values to eq 11. 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, ϕ_{min} is the minimum value of the objective function ϕ defined as

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

where $\eta_k = Q_{calcd} - Q$. Q is the experimental value, and Q_{calcd} is evaluated through eq 13.

Cell Model

An attempt to describe the systems studied in this paper by means of the cell model elaborated by Prigogine and co-

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

function	a_0	a_1	a_2	a_3	$\sigma(Q)$
		DMSO (1) + DMC (2)			
H_m^E/J·mol^{-1}	2442.7	−201.0	1510.4	−422.8	5.2
C_p^E/J·mol^{-1}·K^{-1}	−31.140	−27.929	−12.569		0.0904
V_m^E/cm^3·mol^{-1}	−0.6206	0.4168			0.0010
$\Delta\eta$/mPa·s	−0.9274	−0.3912	−0.1764		0.0013
ΔR/cm^3·mol^{-1}	0.3503	0.0321	0.1269		0.0007
		DMSO (1) + DEC (2)			
H_m^E/J·mol^{-1}	4187.7	−595.0	1696.6		5.6
C_p^E/J·mol^{-1}·K^{-1}	9.2491	132.917	−0.5842	−20.587	0.0233
V_m^E/cm^3·mol^{-1}	−0.7470	0.1476			0.0011
$\Delta\eta$/mPa·s	−0.7912	−0.3279	−0.1792		0.0021
ΔR/cm^3·mol^{-1}	−5.0553	−1.4601			0.0108
		DMSO (1) + PC (2)			
H_m^E/J·mol^{-1}	1651.3	412.6	183.0		2.6
C_p^E/J·mol^{-1}·K^{-1}	−9.7911	13.0960	42.8150	48.2594	0.0196
V_m^E/cm^3·mol^{-1}	1.4737	0.2693			0.0020
$\Delta\eta$/mPa·s	−0.4974	−0.0334	−0.0624		0.0009
ΔR/cm^3·mol^{-1}	−0.6354	−0.0491	−0.0802		0.0014

Table 7. Values of Dipole Moments, μ, and Interaction Energies, E_{ij}/kJ·mol^{-1}, Obtained by Equation 14, with $z = 8$ for DMSO + Esters of Carbonic Acid

	E_{11}	E_{22}	E_{12}	$E_{11} + E_{22} - 2E_{12}$	μ/D
	DMSO (1) + DMC (2), + DEC (2), + PC (2)				
DMC	52.9	36.7	44.6	0.44	3.1[a]
DEC	52.9	43.6	47.9	0.73	0.90[b]
PC	52.9	55.2	107.9	0.29	4.94[b]
DMSO	52.9				4.06[b]

[a] Ref 38. [b] Ref 12.

workers,[32−34] Salsburg and Kirkwood,[35] and Rowlinson[36,37] was carried out, starting from the theoretical expression for H_m^E:

$$H_m^E = x_1x_2E_{11}z[-1.44q + 10.76(RT/zE_{11})^2\,(-2\theta - \delta^2 + 4\delta\theta x_2 + 4x_1x_2\theta^2)] \quad (14)$$

where

$$\delta = (E_{22} - E_{11})/E_{11} \quad (15)$$

$$\theta = (E_{12} - (E_{11} + E_{22})/2)/E_{11} \quad (16)$$

where z is the number of nearest neighbors in the quasi-lattice model, E_{ij} is the interaction energy between molecules i and j, and δ and θ are the normalized parameters. The results do not show any appreciable variation in the range of z values from 8 to 12. Values of δ have been calculated from eq 15 with E_{11} and E_{22} evaluated as the heats of vaporization reported in the literature.[12]

In the case of DMC, E_{22} was obtained from experimental values of vapor pressure,[19] through the Clausius−Clapeyron equation. Table 7 shows the interaction energy values, E_{ij}, between the molecules for the mixtures studied in this paper. The results of comparison between Redlich−Kister and cell model fits is shown in Figure 1 for DMSO + esters of carbonic acid at 298.15 K.

Results and Discussion

Experimental and calculated values of H_m^E, C_p, C_p^E, V_m^E, $\Delta\eta$, and ΔR are graphically represented in Figures 1−6.

Figure 1 shows the values of H_m^E positive for all the binary mixtures of DMSO with esters of carbonic acid (DMC, DEC, and PC). Values of H_m^E are in the order DEC > DMC > PC. To give a qualitative interpretation of the results, we refer to the approximate expression $H_m^E \propto E_{11} + E_{22} - 2E_{12}$, connecting H_m^E to the interaction energies E_{ij} between molecules i and j.

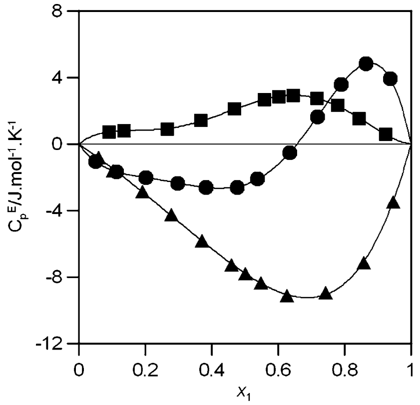

Figure 3. Experimental excess molar heat capacities (C_p^E) for binary mixtures containing DMSO (1) + esters of carbonic acid (2) at 308.15 K. ▲, ■, and ● refer to mixtures containing DMC, DEC, and PC, respectively. Full line, eq 11.

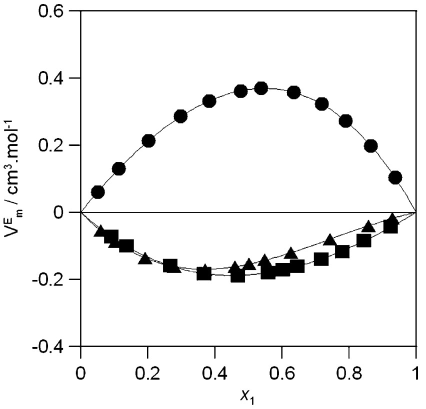

Figure 4. Experimental excess molar volumes (V_m^E) for binary mixtures of DMSO (1) + esters of carbonic acid (2) at 308.15 K. ▲, ■, and ● refer to mixtures containing DMC, DEC, and PC, respectively. Full line, eq 11.

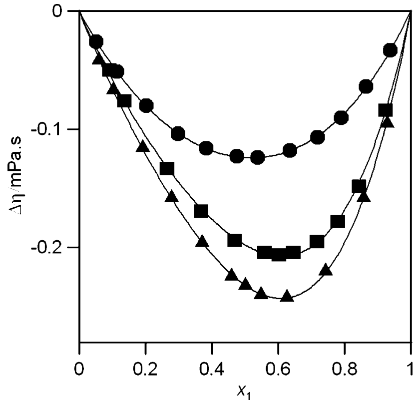

Figure 5. Experimental deviation in viscosities ($\Delta\eta$) for binary mixtures of DMSO (1) + esters of carbonic acid (2) at 308.15 K. ▲, ■, and ● refer to mixtures containing DMC, DEC, and PC, respectively. Full line, eq 11.

Figure 1 shows a decrease of H_m^E proportional to the dipole moment of component 2, and our hypothesis is that larger values of μ, combined with the large μ of DMSO, must lead to a decrease of the difference $E_{22} - 2E_{12}$. Thus H_m^E decreases in the order PC < DMC < DEC, as shown in Table 7 and Figure 1.

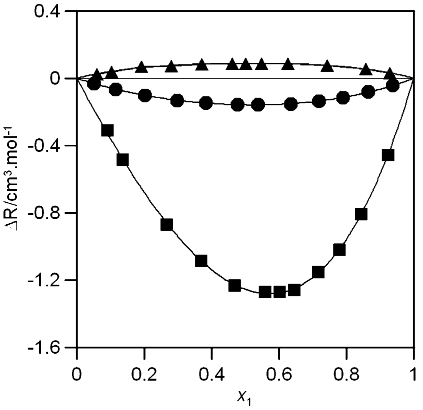

Figure 6. Experimental deviation in refractive indices (ΔR) for binary mixtures of DMSO (1) + esters of carbonic acid (2) at 308.15 K. ▲, ■, and ● refer to mixtures containing DMC, DEC, and PC, respectively. Full line, eq 11.

Values of V_m^E (Figure 4) are negative and close for the mixtures containing DMC and DEC, whereas PC shows marked positive V_m^E values. Volume variations during mixing are connected to interactions between molecules, but here steric effects may play an important role, and the results are of different interpretation. Also, the viscosity data (Figure 5) do not follow the trend observed for the H_m^E values.

The heat capacities of the compounds reported in Figure 2 have a positive dependence on temperature. Only DMC shows a marked increased of C_p with the increase of temperature; the other compounds giving almost linear, parallel curves.

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) 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.

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

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

(6) Annesini, M. C.; De Sanctis, R.; Kikic, I.; Marrelli, R. Excess enthalpy and T−*x* data of aromatic-propylene carbonate mixtures. *J. Chem. Eng. Data* **1984**, *29*, 39−41.

(7) Sharma, P. K.; Narayanan.; Hockey, G. S. NASA’s Jet Propulsion Laboratory, U.S. Patent 6,042,964.

(8) Pistoia, G. *Lithium Batteries: New Materials, Developments and Perspectives*; Industrial Chemical Library, Vol. 5; Elsevier: Amsterdam, 1994.

(9) Tobishima, S.; Arakawa, M.; Yamaki, E. Electrolytic properties of LiClO$_4$−propylene carbonate mixed with amiele-solvents for lithium batteries. *Electrochim. Acta* **1988**, *33*, 239−244.

(10) Gabano, J.-P., Ed. *Lithium Batteries*; Academic Press: New York, 1983.

(11) Nakamura, M.; Chubachi, K.; Tamura, K.; Murakami, K. Excess molar volumes, excess isentropic and isothermal compressibilities, and excess molar isochoric heat capacities of $\{x\mathrm{CF_3CH_2OH} + (1-x)\{\mathrm{HOCN(CH_3)_2}$ or $\mathrm{CH_3CN}\}$ at the temperature 298.15 K. *J. Chem. Thermodyn.* **1993**, *25*, 525−531.

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

(13) Costa, F. S.; Eusebio, M. E.; Redinha, J. S.; Leitao, M. L. P. Enthalpies of solvation of hydroxyl cyclohexane derivatives in different solvents. *J. Chem. Thermodyn.* **1999**, *31*, 895−904.

(14) Aminabhavi, T. M.; Patil, V. B. Density, viscosity, refractive index, and speed of sound in binary mixtures of ethenylbenzene with *N,N*-dimethylacetamide, tetrahydrofuran, *N,N*-dimethylformamide, 1,4-dioxane, dimethyl sulfoxide, chloroform, bromoform, and 1-chloronaphthalene in the temperature interval (298.15−308.15) K. *J. Chem. Eng. Data* **1998**, *43*, 497−503.

(15) Naidu, B. V. K.; Rao, K. C.; Subha, M. C. S. Densities and viscosities of mixtures of some glycols and polyglycols in dimethyl sulfoxide at 308.15 K. *J. Chem. Eng. Data* **2002**, *47*, 379−382.

(16) Ritzoulis, G. Excess properties of the binary liquid systems dimethylsulfoxide + isopropanol and propylene carbonate + isopropanol. *Can. J. Chem.* **1989**, *67*, 1105−1108.

(17) Pereiro, A. B.; Rodriguez, A.; Canosa, J.; Tojo, J. Measurement of the isobaric vapor−liquid equilibria of dimethyl carbonate with acetone, 2-butanone, and 2-pentanone at 101.3 kPa and density and speed of sound at 298.15 K. *J. Chem. Eng. Data* **2005**, *50*, 481−486.

(18) Garcia de la Fuente, I.; Gonzales, J. A.; Cobos, J. C.; Casanova, C. Excess molar volumes for dimethyl carbonate + heptane, decane, 2,2,4-trimethylpentane, cyclohexane, benzene, toluene, or tetrachloromethane. *J. Chem. Eng. Data* **1992**, *37*, 535−537.

(19) *Int. DATA Ser., Sel Data Mixtures, Ser. A* **1991**, 159; *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1993**, 178.

(20) Pardo, J. M.; Tovar, C. A.; Gonzales, D.; Carballo, E.; Romani, L. Thermophysical properties of the binary mixtures diethyl carbonate + (*n*-dodecane or *n*-tetradecane) at several temperatures. *J. Chem. Eng. Data* **2001**, *46*, 212−216.

(21) Mosteiro, L.; Mascato, E.; Cominges, B. E.; Iglesias, T. P.; Legido, J. L. Density, speed of sound, refractive index and dielectric permittivity of (diethyl carbonate + *n*-decane) at several temperatures. *J. Chem. Thermodyn.* **2001**, *33*, 787−802.

(22) Moumouzias, G.; Panopouloa, D. K.; Ritzoulis, G. Excess properties of the binary liquid systems propylene carbonate + acetonitrile. *J. Chem. Eng. Data* **1991**, *36*, 20−23.

(23) 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.

(24) Monk, P.; Wadsö, I. A flow micro reaction calorimeter. *Acta Chem. Scand.* **1968**, *22*, 1842−1852.

(25) Gmehling, I. Excess enthalpies for 1,1,1-trichloroethane with alkanes, ketones, and esters. *J. Chem. Eng. Data* **1993**, *38*, 143−146.

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

(27) Fermeglia, M.; Lapasin, J. Excess volumes and viscosities of binary mixtures of organics. *J Chem. Eng. Data* **1988**, *33*, 415−417.

(28) IUPAC Commission on Atomic Weights and Isotopic Abundances, 1985. *Pure Appl. Chem.* **1986**, *58*, 1677−1692.

(29) Kohlrausch, F. Density of air. *Prakt. Phys.* **1968**, *3*, 40.

(30) Wagenbreth, H.; Blanke, W. Die dichte des wassers im internationalen einheitensystem und in die internationalen praktishen temperaturskala von 1968. *PTB−Mitteilungen* **1971**, *6/71*, 412.

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

(32) Prigogine, I.; Garikian, G. Statistical thermodynamics of binary mixtures. *Physica* **1950**, *16*, 239−248.

(33) Prigogine, I.; Mathot, V. Application of the cell method to the stastistical thermodynamics of solutions. *J. Chem. Phys.* **1952**, *20*, 49−57.

(34) Prigogine, I. *The Molecular Theory of Solutions*; North-Holland: Amsterdam, 1957.

(35) Salsburg, Z. W.; Kirkwood, J. G. The free volume theory of multicomponent fluid mixtures. *J. Chem. Phys.* **1952**, *20*, 1538−1543.

(36) Rowlinson, J. S. The theory of regular solutions. *Proc. R. Soc.* (*London*) **1952**, *A214*, 192−206.

(37) Rowlinson, J. S. Intermolecular forces in CF$_4$ and SF$_6$. *J. Chem. Phys.* **1952**, *20*, 337.

(38) Thiebaut, J.-M.; Rivail, J.-L.; Greffe, J.-L. Dielectric studies of nonelectrolyte solutions. Part 3. Conformational equilibria in 1,2-dichloroethane and dimethyl carbonate. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72* (11), 2024−2034.

Received for review October 21, 2005. Accepted January 3, 2006.

JE050444G