J. Chem. Eng. Data **2003,** *48,* 995−998

Excess Molar Enthalpies of Binary Mixtures Containing Glycols or Polyglycols + Dimethyl Sulfoxide at 308.15 K

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Excess molar enthalpies, H_m^E, were determined as a function of molar fraction at 308.15 K and at atmospheric pressure for the binary mixtures containing dimethyl sulfoxide with ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, poly(ethylene glycol)-200, poly(ethylene glycol)-300, poly(ethylene glycol)-400, and poly(ethylene glycol)-600. All curves are negative over the entire composition range with minima ranging from −430 J·mol^{-1} (propylene glycol) up to −1080 J·mol^{-1} (poly(ethylene glycol)-600). The results were correlated using the Redlich−Kister polynomial, and the adjustable parameters were obtained by the least-squares method. The dependence of H_m^E on mixture composition is qualitatively discussed in terms of molecular interactions.

Introduction

Binary liquid mixtures containing glycols and poly(ethylene glycol)s (PEGs) in nonaqueous solvents are widely used in several processes in the pharmaceutical, petroleum, cosmetic, and food industries.[1] The study of the thermodynamic behavior of these systems and the determination of their physicochemical properties are especially relevant to understanding the type and strength of molecular interactions that can control the mixture behavior. Dimethyl sulfoxide (DMSO) is an aprotic solvent with a reactive S═O group, which can interact with glycols and poly(ethylene glycol)s. These last molecules are usually self-associated by extended networks of intermolecular hydrogen bonds. On mixing, interactions with the S═O group should perturb and disrupt such networks. In the present paper we tried to investigate the type and extent of these interactions by measuring the excess molar enthalpies, H_m^E, of DMSO + ethylene glycol (EG), + propylene glycol (PPG), + diethylene glycol (DEG), + triethylene glycol (TEG), + tetraethylene glycol (TETG), + PEG-200, + PEG-300, + PEG-400, and + PEG-600 at 308.15 K and at atmospheric pressure. Experimental measurements of H_m^E for the binary mixtures studied in this paper have not been found in the literature. However, Naidu et al.[2] have determined densities, viscosities, and excess volumetric properties of some of the mixtures. The consistency of these thermodynamic data is discussed in the present work.

Experimental Section

Chemicals were used without further purification, degassed by ultrasound (ultrasonic bath, Hellma, type 460, Milan, Italy), and dried over molecular sieves (Union Carbide, type 4A, $^1/_{16}$ in. pellets) to reduce the water content before use. The molecular weights of poly(ethylene glycols) were measured by gel permeation chromatography (GPC) and ESI mass spectrometric analysis.[3] The number average, M_n ($=\sum N_iM_i/\sum N_i$), and the weight average, M_w ($=\sum N_iM_i^2/\sum N_iM_i = \sum w_iM_i$), molecular weights were determined. In the above equalities, N_i is the number of moles of species i, having molecular weight M_i and weight fraction w_i. A polydispersity index was obtained as the ratio M_w/M_n. Values of M_n and M_w/M_n are reported in Table 1.

Table 1. Purities, Sources, and Densities, ρ, of Pure Components and Comparisons to Literature Data at 308.15 K

		ρ/g·cm^{-3}	
component	source	expt	lit.
ethylene glycol (+99%)	Aldrich	1.102 93	1.102 94[2] 1.103 1[5]
diethylene glycol (99%)	Aldrich	1.105 65	1.105 57[2] 1.105 78[5]
triethylene glycol (99%)	Aldrich	1.112 10	1.112 09[2] 1.112 7[5]
tetraethylene glycol (99%)	Aldrich	1.112 28	1.112 28[6] 1.113 1[5]
propylene glycol (99.5%)	Riedel-de Haën	1.026 15	1.026 17[2]
PEG-200 (M_n = 192; M_w/M_n = 1.16)	Fluka	1.112 84	1.112 43[2]
PEG-300 (M_n = 274; M_w/M_n = 1.11)	Fluka	1.113 58	1.113 28[2]
PEG-400 (M_n = 365; M_w/M_n = 1.10)	Fluka	1.114 89	1.113 72[6] [a]
PEG-600 (M_n = 554; M_w/M_n = 1.06)	Fluka	1.113 96	
DMSO	Aldrich	1.085 50	1.085 60[2]

[a] At 308.05 K.

Densities, ρ, of pure compounds were determined by a vibrating tube density meter (Anton Paar, model DMA 60/602, Graz, Austria), thermostated by a circulating external bath (Heto, type DTB 623, Copenhagen, Denmark) with a precision of ±0.01 K. The accuracy in density is estimated to be $\pm 1.5 \times 10^{-5}$ g·cm^{-3}. The apparatus and operating procedure were described elsewhere.[4] Purities, sources, and densities of pure substances are given in Table 1 and compared with literature data.[2,5,6]

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10.1021/je034007i CCC: $25.00

The excess molar enthalpies, H_m^E, were measured by using a flow microcalorimeter (LKB Producer AB, model 2107, Bromma, Sweden), equipped with a thermostatic water bath, a digital unit for data acquisition, and two automatic burets (ABU, Radiometer, Copenhagen) to pump pure liquids into the mixing cell of the calorimeter. The water bath controls the temperature of the heat sink, where the mixing and reference cells are located. The accuracy in temperature control is ±0.01 K. Details of the apparatus were reported in previous papers.[7,8]

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

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

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 i-th 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.

The performance and reliability of the calorimeter were checked by the test mixtures hexane + cyclohexane, benzene + cyclohexane, and methanol + water. The corresponding experimental values of H_m^E agreed within 1% with the literature data.[9] Values of H_m^E of all mixtures are reported in Table 2 for different values of x_1, the molar fraction of the glycol. Each set of experimental values of H_m^E was fitted, by an unweighted least-squares method, to a Redlich−Kister polynomial of the type

$$H_m^E(\text{calc}) = x_1 x_2 \sum_{k \geq 0} a_k (x_1 - x_2)^k \tag{3}$$

In eq 3, x_1 and x_2 are the molar fractions of glycols and PEGs (components 1 and 2, respectively), whereas a_k values are adjustable parameters. Values of a_k are reported in Table 3 together with the corresponding standard deviations, $\sigma(H_m^E)$, defined as

$$\sigma(H_m^E) = |\phi_{\min}/(N - n)|^{0.5} \tag{4}$$

where N and n are the numbers of experimental points and of parameters, respectively. $\phi_{\min}$ is the minimum value of the objective function ϕ, defined as

$$\phi = \sum_{k=1}^{N} (H_m^E(\text{calc}) - H_m^E)_k^{\ 2} \tag{5}$$

The data in Table 2 are grouped in Figures 1−3 according to the type of glycol (component 1). In fact, the glycols in Figure 1 (EG and PPG) have two hydroxyl groups, bonded to adjacent carbon atoms. In Figures 2 and 3, the molecular structure of the glycols is characterized by the presence of hydroxyl end groups, separated by increasing numbers of ethylene oxide moieties. Figure 2 reports data for the monodisperse glycols with short chains (DEG, TEG, TETG). In contrast, samples in Figure 3 display a more defined polymeric character. In fact, the relative weight of the hydroxyl end groups in the polymer chain is lower and their effect on the thermodynamic properties is correspondingly less significant. Moreover, sample polydispersity enhances this effect, since it allows for the presence of longer chain tails.

Table 2. Excess Molar Enthalpies, H_m^E, for Binary Mixtures Containing Ethylene Glycol, Propylene Glycol, Diethylene Glycol, Triethylene Glycol, Tetraethylene Glycol, PEG-200, PEG-300, PEG-400, and PEG-600 + Dimethyl Sulfoxide 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}
Ethylene Glycol (1) + Dimethyl Sulfoxide (2)					
0.0506	−195.0	0.3900	−915.8	0.8365	−414.8
0.0963	−367.5	0.4601	−910.2	0.8847	−304.8
0.1378	−499.3	0.5612	−827.7	0.9110	−248.9
0.1757	−613.6	0.6574	−705.1	0.9388	−184.0
0.2423	−757.6	0.7189	−613.8	0.9685	−99.0
0.2989	−850.8	0.7933	−494.7		
Propylene Glycol (1) + Dimethyl Sulfoxide (2)					
0.0389	−81.0	0.3267	−433.7	0.7952	−186.7
0.0748	−163.0	0.3928	−423.4	0.8535	−135.0
0.1082	−222.0	0.4925	−387.5	0.8859	−97.8
0.1392	−270.0	0.5929	−329.9	0.9209	−64.9
0.1921	−354.3	0.6600	−289.3	0.9588	−30.1
0.2444	−402.3	0.7444	−227.2		
Diethylene Glycol (1) + Dimethyl Sulfoxide (2)					
0.0303	−105.2	0.2727	−629.3	0.7500	−467.2
0.0588	−199.0	0.3332	−665.4	0.8182	−380.3
0.0857	−277.8	0.4285	−679.0	0.8571	−319.0
0.1111	−349.0	0.5295	−645.3	0.9000	−250.7
0.1579	−455.7	0.6000	−607.7	0.9474	−145.0
0.2000	−535.9	0.6923	−517.1		
Triethylene Glycol (1) + Dimethyl Sulfoxide (2)					
0.0217	−120.0	0.2104	−756.7	0.6807	−703.3
0.0425	−224.5	0.2621	−830.5	0.7618	−574.5
0.0625	−314.2	0.3477	−897.6	0.8100	−490.5
0.0816	−394.9	0.4444	−897.1	0.8648	−383.7
0.1176	−522.8	0.5160	−864.0	0.9275	−220.1
0.1509	−628.9	0.6153	−777.1		
Tetraethylene Glycol (1) + Dimethyl Sulfoxide (2)					
0.0169	−110.0	0.1709	−739.9	0.6225	−846.2
0.0332	−201.9	0.2155	−838.7	0.7121	−744.0
0.0490	−289.5	0.2919	−922.0	0.7673	−675.5
0.0643	−365.4	0.3818	−950.3	0.8318	−555.9
0.0934	−494.1	0.4519	−945.3	0.9082	−351.1
0.1208	−602.7	0.5529	−904.2		
PEG-200 (1) + Dimethyl Sulfoxide (2)					
0.0171	−104.0	0.1726	−678.8	0.6253	−822.6
0.0336	−197.9	0.2175	−762.2	0.7146	−729.8
0.0496	−277.9	0.2944	−844.5	0.7694	−638.4
0.0650	−346.7	0.3850	−886.4	0.8335	−504.6
0.0944	−463.0	0.4548	−900.6	0.9092	−301.1
0.1221	−556.8	0.5559	−875.5		
PEG-300 (1) + Dimethyl Sulfoxide (2)					
0.0120	−93.3	0.1276	−606.3	0.5392	−981.6
0.0238	−181.7	0.1631	−676.7	0.6371	−925.8
0.0353	−248.2	0.2263	−763.3	0.7006	−836.8
0.0465	−316.9	0.3051	−852.1	0.7783	−666.2
0.0681	−420.1	0.3691	−906.8	0.8753	−390.7
0.0888	−496.9	0.4674	−971.5	0.9035	−310.7
PEG-400 (1) + Dimethyl Sulfoxide (2)					
0.0091	−70.0	0.0990	−554.4	0.4677	−1010.3
0.0180	−149.2	0.1277	−625.3	0.5687	−1035.6
0.0267	−219.9	0.1801	−717.6	0.6374	−991.6
0.0353	−274.8	0.2479	−792.5	0.7250	−867.6
0.0521	−354.6	0.2923	−849.6	0.8406	−565.9
0.0682	−441.7	0.3973	−949.5	0.8755	−460.0
PEG-600 (1) + Dimethyl Sulfoxide (2)					
0.0060	−50.1	0.0675	−442.6	0.3667	−971.8
0.0119	−111.7	0.0880	−517.2	0.4648	−1071.9
0.0178	−167.9	0.1264	−607.2	0.5366	−1081.9
0.0236	−204.5	0.1784	−683.2	0.6346	−999.2
0.0349	−283.5	0.2245	−745.8	0.7765	−685.9
0.0460	−346.9	0.3027	−861.9	0.8224	−580.0

Table 3. Least-Squares Parameters, a_k, Eq 3, and Standard Deviations, $\sigma(H_m^E)$, Eq 5, of Experimental Excess Molar Enthalpies, H_m^E, of Binary Mixtures Containing Glycols and Poly(ethylene glycols) + DMSO at 308.15 K

mixture	a_0	a_1	a_2	a_3	a_4	$\sigma(H_m^E)/J\cdot mol^{-1}$
EG + DMSO	−3538.7	1410.9	−149.3	−1113.7		3.7
DEG + DMSO	−2645.3	893.8	−788.4	−621.5		3.6
TEG + DMSO	−3493.5	1174.9	−1133.5			2.9
TETG + DMSO	−3710.3	979.5	−2030.9			4.4
PPG + DMSO	−1530.9	1036.8	−855.6	−300.8	1096.5	3.2
PEG-200 + DMSO	−3567.0	445.3	−1464.4	984.9	−21.7	2.6
PEG-300 + DMSO	−3931.7	−434.1	−97.7	3003.6	−1807.0	3.1
PEG-400 + DMSO	−4111.3	−876.5	−98.8	3296.8	−2464.4	5.5
PEG-600 + DMSO	−4371.5	−419.7	2761.1	2364.7	−6440.9	6.1

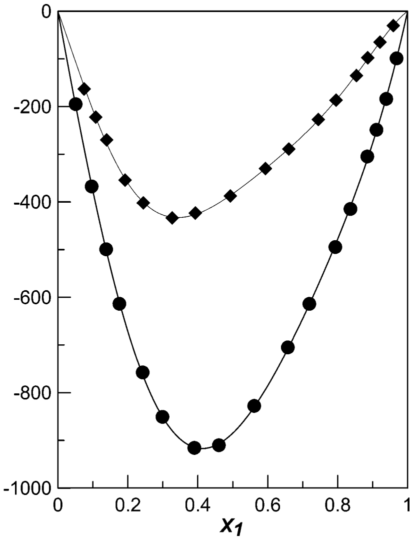

Figure 1. Excess molar enthalpies, H_m^E, for binary mixtures of EG (1) + DMSO (2) (◆) and PPG (1) + DMSO (2) (●) at 308.15 K: solid curves, Redlich−Kister equation.

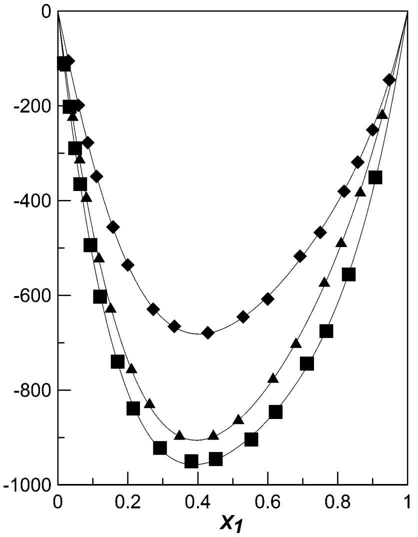

Figure 2. Excess molar enthalpies, H_m^E, for binary mixtures of DEG (1) + DMSO (2) (◆), TEG (1) + DMSO (2) (▲), and TETG (1) + DMSO (2) (■): solid curves, Redlich−Kister equation.

Inspection of Figures 1−3 shows that H_m^E values are negative over the whole mole fraction range. Moreover, the H_m^E values at equimolar composition ($x_1 = 0.5$) vary in the order PPG > EG (Figure 1), DEG > TEG > TETG (Figure 2), and PEG-200 > PEG-300 > PEG-400 > PEG-600 (Figure 3).

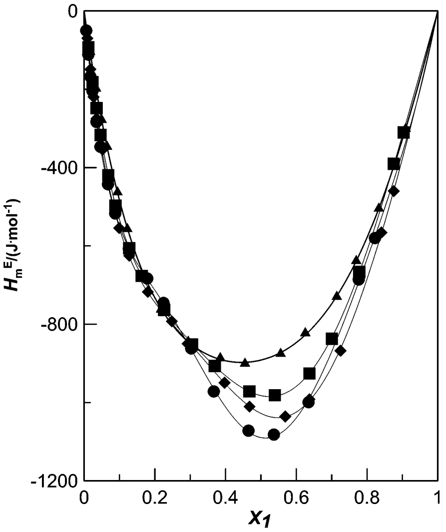

Figure 3. Excess molar enthalpies, H_m^E, for binary mixtures of PEG-200 (1) + DMSO (2) (▲), PEG-300 (1) + DMSO (2) (■), PEG-400 (1) + DMSO (2) (◆), and PEG-600 (1) + DMSO (2) (●) at 308.15 K: solid curves, Redlich−Kister equation.

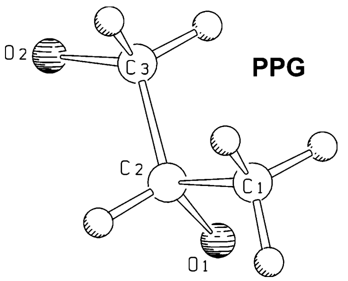

Figure 4. Molecular diagram of propylene glycol with hydroxyl H atoms omitted.

It can be assumed that, as a first approximation, $H_m^E \propto E_{11} + E_{22} - 2E_{12}$, where E_{ij} is the interaction energy between molecules of types i and j. Thus, negative values of H_m^E correspond to $2E_{12} > E_{11} + E_{22}$. Data in Figure 1 suggest that E_{ij} is larger (H_m^E is more negative) for the EG−DMSO mixture as compared to PPG−DMSO. This can be attributed to a lower degree of H-bonding between the components due to the steric hindrance of the methyl group that screens the O1 atom in PPG (Figure 4). Actually, a solid-state X-ray analysis performed by us on literature data[10] shows that DMSO solvates in the crystal, engaging the O2 atom. Moreover, the more and more negative values of H_m^E shown by DEG, TEG, and TETG mixtures with DMSO (Figure 2) are consistent with the increasing contribution of the ethereal groups of glycols to the interaction energy, E_{12}. Both ^{1}H NMR spectroscopy and solid-state X-ray crystallography emphasize that DMSO gives interactions of the type R−C−H···O=S.[11] These interactions become more important when R is substituted by an O atom, as in oxyethylene glycols (Figures 2 and 3), due to the increasing electronegativity of the ethereal group. The same trends are observed in the mixtures of PEGs + DMSO

(Figure 3). Moreover, data in Table 2 and Figure 3 show that TETG and PEG-200 have similar values of H_m^E. The molecular weight of TETG is 194, almost equal to 192, the M_n value of PEG-200. This correlation supports the hypothesis that oxyethylene glycol average molecular weight, as proportional to the number of the repeating units $(OCH_2\text{-}CH_2)_n$ present in the chain, can be considered the major factor to control changes in E_{12}.

The H_m^E data of this paper are in good agreement with the viscosimetric data reported in ref 2, for the same mixtures at the same temperature. Viscosity deviations, $\Delta\eta$, are expected to increase as the strength of molecular interactions is increased by addition of the second component. Actually, inverse correlations between $\Delta\eta$ and H_m^E are observed.[2] Moreover, in all mixtures of DMSO with glycols of types 2 and 3 (oxyethylenic glycols), $\Delta\eta$ increases as the chain length of the glycol is increased. This trend can be explained by the "bridge effect" of the solvent between oxyethylene moieties and hydroxyl groups. In fact, extended Hückel calculations on the DMSO molecule, performed by us, show highly localized charges on O and S atoms (−1.42 and +1.36 e, respectively). This result agrees with the large dipole moment ($\mu = 3.96(4)$ D) of the molecule. As a consequence, DMSO could act as a bidentate ligand, engaging its negative O in H-bonds and the positive S atom in polar interactions with the negatively charged ethereal groups.

In contrast, the mixtures of EG and PPG with DMSO display a direct correlation between $\Delta\eta$ and H_m^E. Actually, viscosity deviations of EG and PPG are very close but vary in the order PPG > EG. In this case, the CH_3 group of PPG seems to provide opposite contributions to viscosity (larger hindrance to viscous flow) as compared to calorimetry (a smaller value of E_{12} than that for the EG molecule).

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Received for review January 9, 2003. Accepted May 7, 2003.

JE034007I