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Excess Molar Enthalpies and Hydrogen Bonding in Binary Mixtures Containing Glycols or Poly(Ethylene Glycols) and 2-Phenylethyl Alcohol at 308.15 K and Atmospheric Pressure

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Excess molar enthalpies, H_m^E, of binary liquid mixtures containing as component 1 ethylene glycol, propylene glycol, di(ethylene glycol), tri(ethylene glycol), tetra(ethylene glycol), or some PEGs, such as PEG200, PEG300, PEG400, PEG600, and 2-phenylethyl alcohol (2), have been measured over the entire range of mole fraction x_1 at 308.15 K and at atmospheric pressure, using a flow microcalorimeter. The values of H_m^E vary from a value of −600 J·mol^{-1} (mixture containing PEG600) up to a maximum of 254 J·mol^{-1} (mixture containing propylene glycol) decreasing as the chain length of glycols or PEGs increase. Curves are not symmetric, and in the case of mixtures containing PEGs, an intersection among the curves at $x_1 \approx 0.65$ has been observed. Results were fitted to the Redlich−Kister polynomial to estimate the adjustable parameters and the standard deviations between experimental and calculated values. Qualitative discussion of H bonding in the liquid state is given.

Introduction

Poly(ethylene glycols) (PEGs) are linear or branched, neutral poly(ethers), available in a variety of M_Ws and soluble in most organic solvents and are widely used in the pharmaceutical, chemical, and cosmetic industries, in the purification of biological materials, and as additives in the food industry.[1−4] Ethylene and propylene glycols were studied to complete the series.

Besides, accurate measurements of experimental data of physical properties, as excess molar enthalpy, in mixtures of organic liquids, are required for a full understanding of their thermodynamic behavior.

Continuing our previous studies,[5−9] we report in this paper the excess molar enthalpies, H_m^E, of binary mixtures containing ethylene glycol (EG), propylene glycol (PPG), di(ethylene glycol) (DEG), tri(ethylene glycol) (TEG), tetra(ethylene glycol) (TETG), or some PEGs such as PEG200, PEG300, PEG400, PEG600, or 2-phenylethyl alcohol at 308.15 K and at atmospheric pressure. In all cases, the whole range of the mixture composition was covered. In this work, 2-phenylethyl alcohol has been chosen since it is the next higher homologue of benzyl alcohol, which was recently studied by us.[9] Aryl alcohols are solvents of particular interest since they are flexible organic molecules presenting a conformational complexity. The aim is to study the influence on the H_m^E of the increasing of n in the aryl alcohols Ph−(CH$_2$)$_n$−OH and to obtain information about the interaction of phenylethyl alcohol with glycols or PEGs, which are self-associated through hydrogen bonding.[10]

Glycols and PEGs are component 1, whose formula has been expressed as $HOCH_2-[OP]_p-CH_2OH$, where OP is the repeating ethereal unit CH_2OCH_2. The values of p are reported in Table 1 and range between zero (EG and PPG) and 11.17 (PEG600).

Table 1. Data of Pure Components

compound	M_n	p	T/(K)	ρ/(g·cm^{-3}) exp	ρ/(g·cm^{-3}) lit
ethylene glycol	62.07	0	298.15	1.10980	1.10982[9]
			308.15	1.10293	1.1029[8]
propylene glycol	76.10	0	308.15	1.02615	1.02617[8]
diethylene glycol	106.12	1	298.15	1.11238	1.11233[11]
			308.15	1.10588	1.1057[10]
triethylene glycol	150.17	2	298.15	1.11978	1.11976[11]
			308.15	1.11261	1.1120[8]
tetraethylene glycol	194.23	3	298.15	1.12009	1.12005[9]
PEG P-200	$M_n = 192$; $M_w/M_n = 1.16$	2.95	308.15	1.113001	1.1124[8]
PEG P-300	$M_n = 274$; $M_w/M_n = 1.11$	4.81	308.15	1.11391	1.1132[8]
PEG P-400	$M_n = 365$; $M_w/M_n = 1.10$	6.88	308.15	1.11413	1.11372[10]
PEG P-600	$M_n = 554$; $M_w/M_n = 1.06$	11.17	308.15	1.11440	
2-phenylethyl alcohol	122.17		308.15	1.00868	

Experimental Section

Chemicals used in this work were obtained from Aldrich, Fluka, and Riedel-de-Haen, analytical grade, with purities ≥99%. Substances were kept over freshly activated molecular sieves (Union Carbide type 4A) for several days before use, to reduce the water content, and were protected from atmospheric moisture and carbon dioxide. After this treatment, the content of water, as determined by gas−liquid chromatography analysis, was ≤0.01 mass %. Before use, pure liquids were also degassed by ultrasound (ultrasonic bath, Hellma, type 460, Milan, Italy).

The molecular weights of PEGs were obtained by gel permeation chromatography as described in a previous

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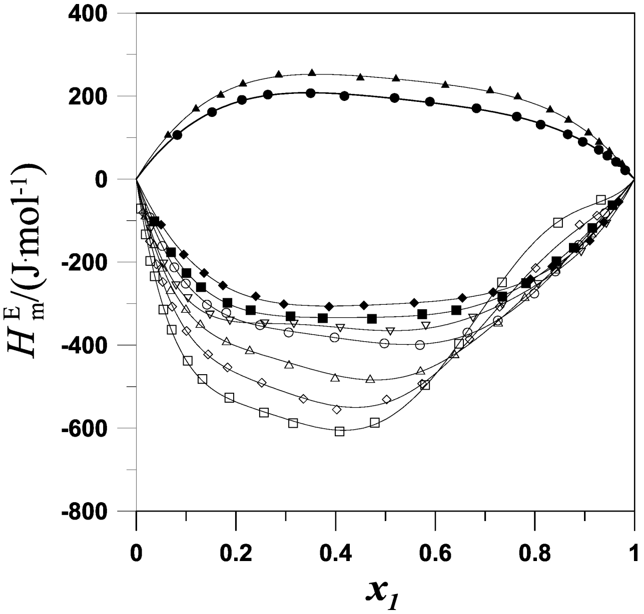

Figure 1. Excess molar enthalpies, H^E_m, at 308.15 K, for binary mixtures of ●, EG (1) + 2-phenylethyl alcohol (2); ▲, PPG (1) + 2-phenylethyl alcohol (2); ◆, DEG (1) + 2-phenylethyl alcohol (2); ■, TEG (1) + 2-phenylethyl alcohol (2); ○, TETG (1) + 2-phenylethyl alcohol (2); ▽, PEG200 (1) + 2-phenylethyl alcohol (2); △, PEG300 (1) + 2-phenylethyl alcohol (2); ◇, PEG400 (1) + 2-phenylethyl alcohol (2); □, PEG600 (1) + 2-phenylethyl alcohol (2). Solid curves are values obtained from the Redlich–Kister equation (eq 1).

paper.[5] Both the number average, M_n ($\Sigma N_iM_i/\Sigma N_i$), and the weight average, M_w ($\Sigma N_iM_i^2/\Sigma N_iM_i = \Sigma w_iM_i$), molecular weights were determined, where 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 where also density values, ρ, in comparison with literature data,[8–11] are shown.

Densities of pure compounds were measured using a vibrating-tube density meter (Anton Paar, model DMA 60/602, Graz, Austria) operating under static mode. The temperature inside the vibrating-tube cell was measured using a digital thermometer (Anton Paar, type CTK 100) and was regulated better than ±0.01 K, using a water-circulating bath (Heto, type 01 DBT 623, Bireròd, Denmark). The uncertainty in the density was $\pm 1.5 \times 10^{-5}$ g·cm^{-3}.

Calorimetric Measurements. The excess molar enthalpies, H^E_m, were measured by a flow isothermal microcalorimeter (LKB, model 2107, Producer AB, Bromma, Sweden), which consists of a 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 located. The temperature of the bath is controlled to within ±0.01 K. The pure components are pumped into the mixing cell at selected flow rates. Molar fractions of mixtures in the mixed stream were calculated from densities and volumetric flow rates of components. The total flow rates are usually kept at about 0.4 cm^3·min^{-1}, but in dilute regions, the total flow rates may increase up to 0.8 cm^3·min^{-1}. Details and operating procedures of the apparatus have been reported elsewhere.[12,13] The uncertainty of the reported H^E values was checked by measurements on three standard systems, cyclohexane + hexane, benzene + cyclohexane, and methanol + water at 298.15 K. Agreement with literature data[14] is better than 0.5% at the maximum of the thermal effect.

Table 2. Excess Molar Enthalpies, H^E_m, for Binary Mixtures Containing Ethylene Glycol or Propylene Glycol or Di(Ethylene Glycol) or Tri(Ethylene Glycol) or Tetra(Ethylene Glycol) or PEG200, PEG300, PEG400, or PEG600 (Component 1) + 2-Phenylethyl Alcohol (Component 2) at 308.15 K

x_1	H^E_m J·mol^{-1}	x_1	H^E_m J·mol^{-1}	x_1	H^E_m J·mol^{-1}
Ethylene Glycol + 2-Phenylethyl Alcohol					
0.0823	106.1	0.5183	195.4	0.8959	89.7
0.1521	161.3	0.5892	186.4	0.9281	70.5
0.2120	190.8	0.6827	170.5	0.9451	56.2
0.2640	203.4	0.7635	150.5	0.9627	41.4
0.3498	206.9	0.8115	131.0	0.9810	21.2
0.4177	200.1	0.8659	107.6		
Propylene Glycol + 2-Phenylethyl Alcohol					
0.0637	105.2	0.4495	243.6	0.8672	142.0
0.1198	168.7	0.5212	241.0	0.9074	111.3
0.1695	202.1	0.6201	225.6	0.9289	88.7
0.2139	229.2	0.7101	212.8	0.9494	66.3
0.2858	250.8	0.7656	197.9	0.9751	35.7
0.3525	254.5	0.8305	166.3		
Di(Ethylene Glycol) + 2-Phenylethyl Alcohol					
0.0500	−110.1	0.3869	−307.6	0.8347	−210.4
0.0952	−181.7	0.4569	−304.3	0.8834	−167.7
0.1363	−226.2	0.5579	−298.1	0.9099	−148.7
0.1738	−256.3	0.6544	−286.2	0.9381	−103.6
0.2399	−282.4	0.7163	−272.8	0.9680	−55.0
0.2961	−301.6	0.7911	−241.6		
Tri(Ethylene Glycol) + 2-Phenylethyl Alcohol					
0.0360	−102.1	0.3096	−330.4	0.7820	−250.9
0.0695	−176.3	0.3741	−335.2	0.8433	−198.1
0.1008	−226.8	0.4728	−336.8	0.8777	−165.7
0.1300	−260.3	0.5737	−325.5	0.9150	−118.1
0.1832	−298.2	0.6421	−315.8	0.9556	−63.1
0.2296	−316.0	0.7346	−282.8		
Tetra(Ethylene Glycol) + 2-Phenylethyl Alcohol					
0.0281	−121.0	0.2575	−348.1	0.7351	−303.0
0.0546	−204.2	0.3161	−349.2	0.8063	−253.5
0.0797	−256.7	0.4095	−359.2	0.8473	−212.2
0.1036	−287.5	0.5099	−367.2	0.8928	−175.9
0.1478	−327.2	0.5811	−353.7	0.9433	−108.1
0.1878	−341.7	0.6754	−334.6		
PEG200 + 2-Phenylethyl Alcohol					
0.0268	−92.0	0.2483	−352.1	0.7255	−340.9
0.0522	−161.3	0.3058	−369.6	0.7986	−275.8
0.0763	−212.8	0.3979	−381.8	0.8409	−222.6
0.0992	−251.8	0.4978	−395.9	0.8880	−158.8
0.1418	−302.7	0.5693	−399.9	0.9407	−82.0
0.1805	−322.1	0.6647	−369.8		
PEG300 + 2-Phenylethyl Alcohol					
0.0181	−87.0	0.1811	−389.9	0.6389	−421.2
0.0355	−155.9	0.2277	−411.2	0.7264	−344.9
0.0524	−212.7	0.3066	−446.1	0.7797	−283.8
0.0687	−266.9	0.3989	−477.9	0.8415	−217.1
0.0996	−311.8	0.4694	−480.8	0.9139	−130.1
0.1285	−348.0	0.5703	−460.9		
PEG400 + 2-Phenylethyl Alcohol					
0.0138	−81.0	0.1440	−422.6	0.5738	−493.0
0.0273	−149.8	0.1832	−453.9	0.6688	−385.5
0.0404	−205.2	0.2517	−490.7	0.7292	−307.7
0.0531	−248.1	0.3355	−529.5	0.8015	−214.4
0.0720	−307.6	0.4023	−555.3	0.8898	−110.1
0.1009	−365.9	0.5024	−530.9		
PEG600 + 2-Phenylethyl Alcohol					
0.0095	−71.3	0.1030	−437.8	0.4787	−586.9
0.0188	−133.3	0.1327	−481.5	0.5794	−496.4
0.0279	−196.9	0.1866	−526.9	0.6474	−396.9
0.0368	−234.4	0.2561	−562.3	0.7337	−248.6
0.0543	−314.1	0.3146	−588.0	0.8464	−105.1
0.0711	−362.9	0.4078	−608.1		

Table 3. Least-Squares Parameters, a_k, Eq 1, and Standard Deviations, (σH^E_m) of Binary Mixtures Containing Ethylene Glycol, Propylene Glycol, Di(Ethylene Glycol), Tri(Ethylene Glycol), Tetra(Ethylene Glycol), PEG200, PEG300, PEG400, or PEG600 (Component 1) + 2-Phenylethyl Alcohol (Component 2) at 308.15 K

mixture	a_0	a_1	a_2	a_3	a_4	$\sigma(H^E_m)/(\text{J·mol}^{-1})$
ethylene glycol + 2-phenylethyl alcohol	785.1981	−242.3428	619.1903			2.13
propylene glycol + 2-phenylethyl alcohol	973.1081	−215.1297	795.2099			2.49
diethylene glycol + 2-phenylethyl alcohol	−1207.3958	111.3945	−1052.6210	193.0004		3.08
triethylene glycol + 2-phenylethyl alcohol	−1329.6374	58.2981	−1049.5068	850.5795		2.11
tetraethylene glycol + 2-phenylethyl alcohol	−1460.8442	−51.5345	−548.6929	1396.8525	−1694.7233	3.26
PEG200 + 2-phenylethyl alcohol	−1576.4964	−190.8632	−931.2762	1491.5769		3.39
PEG300 + 2-phenylethyl alcohol	−1932.3430	189.7690	401.2572	1502.7521	−2210.2262	4.74
PEG400 + 2-phenylethyl alcohol	−2156.8983	742.3456	1169.4928	1630.6745	−2971.5766	4.41
PEG600 + 2-phenylethyl alcohol	−2315.8856	1316.4318	2051.3613	1932.1218	−4403.7155	4.80

Results and Discussion

Values of H^E_m of all mixtures are reported in Figure 1 and in Table 2 as a function of x_1. Experimental enthalpies were fitted by the method of least squares, with all points weighted equally, to the smoothing Redlich−Kister equation

$$H^E_m(\text{calc})/(\text{J·mol}^{-1}) = x_1 x_2 \sum_{k\geq 0} a_k (x_1 - x_2)^k \qquad (1)$$

The resulting adjustable parameters, a_k, and the standard deviations, $\sigma(H^E_m)$, are reported in Table 3 and were obtained following the procedure described elsewhere.[9] In general, the data show a decrease of H^E_m with an increase of the molecular weight of component 1. The same trend has been observed for the mixtures cellosolve + 1-butanol[17] and for glycols (or PEGs) + 3-pheylpropyl alcohol.[16] Moreover, the H^E_ms of mixtures with EG and PPG (both with $p = 0$) are positive, whereas those of the other mixtures ($p > 0$) are negative. We note that, in the case of $p = 0$, the above-mentioned rule of the molecular weight fails, since H^E_m is smaller for the mixtures containing EG. This inversion has been just observed by us in a previous work[8] and can be attributed to the steric hindrance of the methyl group present in PPG. It is of some interest to examine the values of H^E_m obtained for mixtures with the same glycol and with a different alcohol, i.e., 2-phenylethyl alcohol, in the present work, and benzyl alcohol.[9] The comparison shows that, for EG, the enthalpies of mixing are roughly the same, while for $p > 0$, the absolute values of H^E_m for 2-phenylethyl alcohol are about half as large as those with benzyl alcohol. These results can be better shown in Figure 2, where the ΔH^E_m values, calculated at $x_1 = 0.4$, between the H^E_m value of a mixture containing 2-phenylethyl alcohol and benzyl alcohol, are reported as a function of p and can be qualitatively explained allowing for both the structural differences between the two alcohols and the hydrogen bond interactions in the liquid state. Bearing in mind the approximated expression $H^E_m \propto E_{11} + E_{22} - 2E_{12}$, in which E_{ij} are the interaction energies between molecules i and j, the ΔH^E_ms are proportional to $E_{22} - 2E_{12}$. This difference, as said, results larger when the solvent is 2-phenylethyl alcohol. Concerning the term E_{22}, actually, ab initio data testify the self-association of benzyl alcohol with formation of dimers stabilized by both OH···O and OH···π H bonds.[17,18] However, it was observed[18] that the strength of the OH···π interaction decreases with an increase in the length of the alkyl chain linked to the hydroxyl group of the alcohol. Thus, if this type of dimer formation can be assumed for the 2-phenylethyl alcohol, too, the OH···OH bond strength, and then E_{22}, is larger for benzyl alcohol than for 2-phenylethyl alcohol. However, when we examine the mixtures EG + alcohols, with no ethereal group in the glycol chain ($p = 0$), the difference $E_{22} - 2E_{12}$ involves only the OH···OH interactions in pure alcohol and those between alcohol and glycol (yielding two OH groups). These interactions balance, leading to values of H^E_m depending substantially on E_{11} and thus nearly the same for both the systems EG + alcohol.

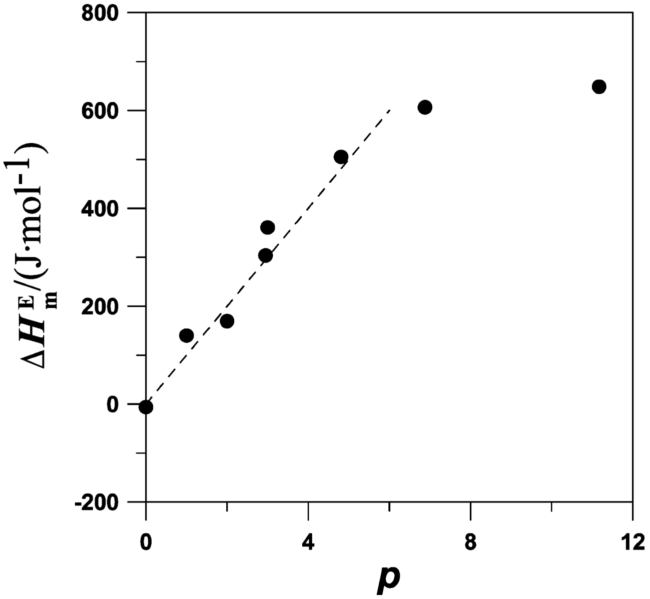

Figure 2. Differences ΔH^E_m, calculated at $x_1 = 0.4$, between H^E_m of mixtures containing 2-phenylethyl alcohol (this work) and benzyl alcohol[9] as a function of the number p of ethereal groups contained in the same component 1.

Instead, for $p > 0$, the increase of p and the consequent increase of E_{12} leads to H^E_m more and more negative (Figure 1), whereas the ΔH^E_ms (Figure 2) indicate that the ethereal groups of glycols or PEGs are less accessible to O−H group of the 2-phenylethyl alcohol than of benzyl alcohol. This steric effect can be evaluated about 100 J/mol for $p \leq 6$. For larger values of p, ΔH^E_m tends to an asymptotic value signifying a saturation effect, due to the lesser availability of the ethereal O of PEGs when the chain is longer, that is farther and farther from the linear pattern.[19]

Finally, it must be noted that the H^E_m curve (Figure 1), relative to the system PEG600/2-phenylethyl alcohol for $x_1 > 0.65$, becomes less negative than the other curves. This effect has been observed also in binary systems containing benzyl alcohol,[9] but in latter cases, at $x_1 = 0.8$, the H^E_m curve of PEG600 becomes less negative only of PEG400 and PEG300.

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