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Excess molar enthalpies and hydrogen bonding in binary mixtures containing glycols or poly(ethylene glycols) and 3-phenylpropyl alcohol at 308.15 K and atmospheric pressure

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Abstract

Excess molar enthalpies, H_m^E, of binary liquid mixtures containing ethylene glycol (EG), propylene glycol (PPG), di(ethylene glycol) (DEG), tri(ethylene glycol) (TEG), tetra(ethylene glycol) (TETG), or some PEGs, as PEG200, PEG300, PEG400, PEG600, +3-phenylpropyl alcohol (PPAL) have been measured over the entire range of composition at 308.15 K and at atmospheric pressure, using a flow microcalorimeter.

The H_m^E's vary from a value of $-200\,\mathrm{J\,mol^{-1}}$ (mixture containing PEG600 or DEG) up to a maximum of $350\,\mathrm{J\,mol^{-1}}$ (mixture containing propylene glycol), decreasing as the chain length of PEGs increases. Curves are not symmetric and, in the case of mixtures containing PEGs, an intersection among the curves 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. The results are discussed in term of both intermolecular H-bonding and variation in molecular conformation of PEGs.

Keywords: Molar enthalpy; Binary liquid mixtures; H-bonding

1. Introduction

Poly(ethylene glycols) (PEGs) are linear or branched, neutral poly(ethers), available in a variety of Mws and soluble in most organic solvents, and are widely used in the pharmaceutical, chemical and cosmetic industry, in the purification of biological materials and, as additive, in food industry [1–4].

Continuing our previous studies [5–10], 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) (TTEG), and some PEGs, as PEG200, PEG300, PEG400, PEG600, +3-phenylpropyl alcohol (PPAL) at 308.15 K and at atmospheric pressure. In all cases, the whole range of mixture composition was covered. The aim is to study the influence on 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 alcohols with glycols or PEGs, which are self-associated through hydrogen bonding [11]. In this work, the aryl alcohol with $n = 3$ is considered. The homologous alcohols with $n = 1$, benzyl alcohol (BA), and $n = 2$, 2-phenylethyl alcohol (PEAL), have been studied in previous works [9,10].

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 0 (EG and PPG) and 11.17 (PEG600).

2. Experimental

Details on the chemicals used and check of purity are given in [10], reporting also the method for the determination of molecular weight averages and polydispersivity of PEGs.

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Table 1
Data of pure components

Compound	M_n	p	T (K)	ρ (g cm^{-3})	
				Experimental	Literature
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]
Di(ethylene glycol)	106.12	1	298.15	1.11238	1.11233 [12]
			308.15	1.10588	1.1057 [11]
Tri(ethylene glycol)	150.17	2	298.15	1.11978	1.11976 [12]
			308.15	1.11261	1.1120 [8]
Tetra(ethylene glycol)	194.23	3	298.15	1.12009	1.12005 [9]
PEG200	$M_n = 192$; $M_w/M_n = 1.16$	2.95	308.15	1.113001	1.1124 [8]
PEG300	$M_n = 274$; $M_w/M_n = 1.11$	4.81	308.15	1.11391	1.1132 [8]
PEG400	$M_n = 365$; $M_w/M_n = 1.10$	6.88	308.15	1.11413	1.11372 [11]
PEG600	$M_n = 554$; $M_w/M_n = 1.06$	11.17	308.15	1.11440	–
3-Phenylpropyl alcohol	136.20	–	308.15	0.99078	–

Densities of pure compounds ρ 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}. Table 1

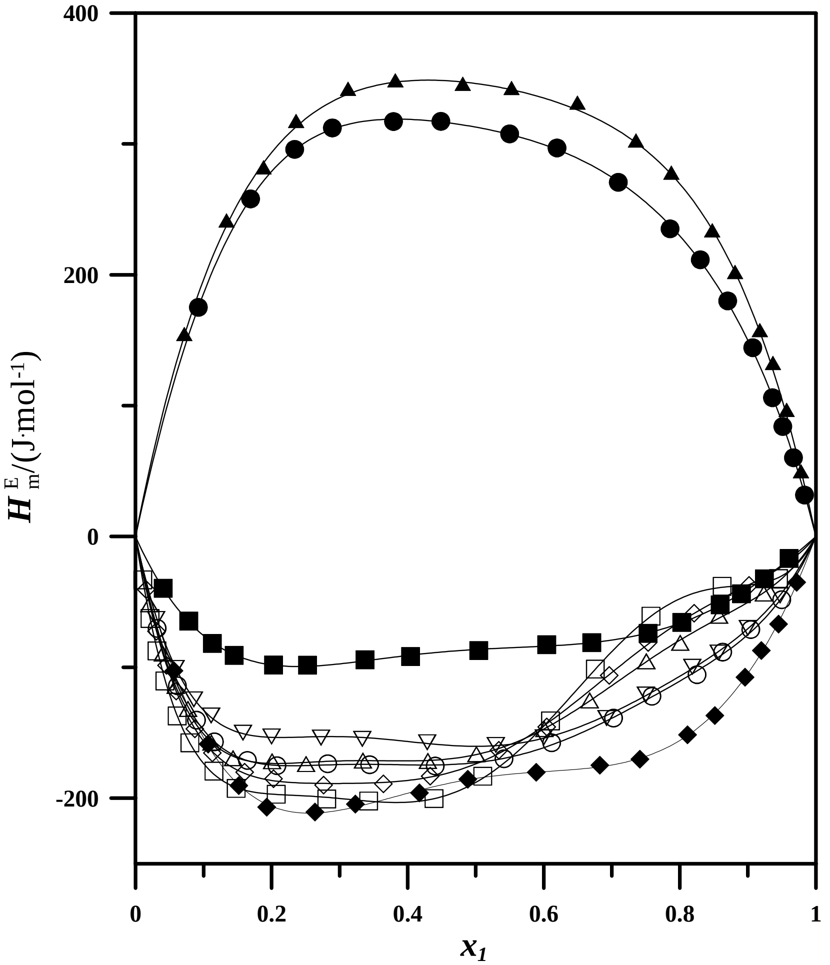

Fig. 1. Excess molar enthalpies, H^E_m, at 308.15 K, for binary mixtures of: (●) EG (1) + 3-phenylpropyl alcohol (2); (▲) PPG (1) + 3-phenylpropyl alcohol (2); (■) DEG (1) + 3-phenylpropyl alcohol (2); (◆) TEG (1) + 3-phenylpropyl alcohol (2); (▽) TETG (1) + 3-phenylpropyl alcohol (2); (○) PEG200 (1) + 3-phenylpropyl alcohol (2); (◇) PEG300 (1) + 3-phenylpropyl alcohol (2); (△) PEG400 (1) + 3-phenylpropyl alcohol (2); (□) PEG600 (1) + 3-phenylpropyl alcohol (2). Solid curves, Redlich–Kister equation (1).

Table 2
Excess molar enthalpies

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) + phenylpropyl alcohol (2)					
0.0924	175.1	0.5498	307.7	0.9072	144.3
0.1691	258.0	0.6195	296.9	0.9361	106.0
0.2339	295.8	0.7095	270.7	0.9513	84.1
0.2893	312.2	0.7857	235.1	0.9670	60.2
0.3791	317.1	0.8301	211.5	0.9832	31.7
0.4488	317.3	0.8703	180.0	–	–
Propylene glycol (1) + phenylpropyl alcohol (2)					
0.0717	153.0	0.4810	344.3	0.8812	200.4
0.1338	239.8	0.5526	341.0	0.9175	156.0
0.1881	280.4	0.6496	329.8	0.9368	130.9
0.2360	315.8	0.7356	300.9	0.9570	95.1
0.3123	340.4	0.7876	276.3	0.9780	48.1
0.3819	346.9	0.8476	232.3	–	–
Di(ethylene glycol) (1) + phenylpropyl alcohol (2)					
0.0563	−102.6	0.4173	−196.0	0.8514	−136.8
0.1066	−158.6	0.4884	−185.5	0.8958	−107.5
0.1519	−190.3	0.5889	−180.2	0.9197	−87.1
0.1927	−206.8	0.6825	−174.8	0.9450	−66.9
0.2637	−210.5	0.7413	−170.1	0.9717	−35.0
0.3232	−204.5	0.8112	−151.6	–	–
Tri(ethylene glycol) (1) + phenylpropyl alcohol (2)					
0.0407	−39.6	0.3373	−94.2	0.8029	−65.6
0.0782	−64.6	0.4042	−91.7	0.8593	−52.2
0.1129	−81.7	0.5045	−87.2	0.8906	−43.7
0.1450	−90.9	0.6044	−82.6	0.9244	−32.3
0.2029	−98.2	0.6706	−81.0	0.9607	−16.7
0.2528	−98.3	0.7534	−74.0	–	–
Tetra(ethylene glycol) (1) + phenylpropyl alcohol (2)					
0.0318	−70.2	0.2824	−173.7	0.7590	−122.1
0.0616	−114.0	0.3441	−174.4	0.8253	−105.6
0.0896	−140.3	0.4405	−175.4	0.8630	−88.3
0.1160	−156.9	0.5416	−169.9	0.9043	−71.1
0.1644	−171.1	0.6116	−157.6	0.9497	−48.3
0.2079	−175.1	0.7025	−138.7	–	–
PEG200 (1) + phenylpropyl alcohol (2)					
0.0303	−63.1	0.2727	−153.8	0.7500	−120.9
0.0588	−100.5	0.3334	−154.8	0.8182	−99.7
0.0857	−124.6	0.4287	−157.3	0.8571	−88.8
0.1111	−136.9	0.5295	−159.4	0.9000	−69.9
0.1579	−150.0	0.6000	−153.5	0.9474	−45.1
0.2000	−152.9	0.6923	−138.8	–	–
PEG300 (1) + phenylpropyl alcohol (2)					
0.0205	−51.7	0.2007	−171.6	0.6676	−125.1
0.0402	−89.3	0.2507	−173.8	0.7508	−95.3
0.0591	−114.0	0.3342	−171.1	0.8007	−81.1
0.0772	−131.6	0.4297	−171.4	0.8577	−60.4
0.1115	−157.4	0.5010	−166.3	0.9234	−43.4
0.1434	−169.3	0.6010	−147.1	–	–
PEG400 (1) + phenylpropyl alcohol (2)					
0.0157	−40.5	0.1604	−180.1	0.6044	−145.5
0.0308	−72.4	0.2029	−185.1	0.6962	−106.1
0.0456	−98.5	0.2764	−190.0	0.7534	−81.0
0.0598	−118.1	0.3643	−189.0	0.8209	−58.6
0.0872	−147.0	0.4331	−183.1	0.9017	−37.3
0.1129	−165.4	0.5340	−163.3	–	–
PEG600 (1) + phenylpropyl alcohol (2)					
0.0107	−33.1	0.1153	−179.3	0.5103	−183.2
0.0213	−62.6	0.1479	−192.5	0.6099	−140.9
0.0315	−87.4	0.2067	−197.0	0.6758	−101.3
0.0432	−110.4	0.2811	−200.6	0.7577	−60.9
0.0612	−137.1	0.3426	−202.1	0.8621	−38.0
0.0799	−157.6	0.4387	−200.3	0.945	−32.13

H_m^E for binary mixtures containing: ethylene glycol or propylene glycol or di(ethylene glycol) or tri(ethylene glycol) or tetra(ethylene glycol) or PEG200 or PEG300 or PEG400 or PEG600 (component 1) + 3-phenylpropyl alcohol (component 2) at 308.15 K.

shows the value of ρ, in comparison with the literature data [8–12]. Also values of molecular weight averages of PEGs are given, taken from the above mentioned paper.

The excess molar enthalpies, H_m^E, were measured by a flow isothermal microcalorimeter LKB, model 2107 (twin cells system, balancing the friction heat losses), Producer AB, Bromma, Sweden, which consists of a mixing cell, a reference cell, a thermostatic water bath, a data acquisition unit, and two liquid burettes (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. Molar fractions of mixtures in the mixed stream were calculated from densities and volumetric flow rates of components pumped into the mixing cell. The total flow rates never exceed 0.8 cm^3 min^{-1}. Details and operating procedure of the apparatus have been reported elsewhere [13,14]. The uncertainty of the experimental H_m^E values is of the order 1%. Our equipment was checked by measurements on the three standard systems, cyclohexane + hexane, benzene + cyclohexane, and methanol + water at 298.15 K. Agreement with literature data [15] is better than 0.5% at the maximum of the thermal effect.

3. Results and discussion

Values of H_m^E of all mixtures are reported in Fig. 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:

$$H_m^E(\text{calc}) = x_1 x_2 \sum_{k\geq 0} a_k \, (x_1 - x_2)^k \qquad (1)$$

The resulting adjustable parameters, a_k, and the standard deviations, $\sigma(H_m^E)$, are given in Table 3 and were obtained following the procedure described elsewhere [8]. In general, the data show decreasing of H_m^E with the increasing of molecular weight of component 1. Moreover, the H_m^E's of mixtures with EG and PPG (both with $p = 0$) are positive, whereas those of the other mixtures with $p > 0$ are negative. These results confirm the trends for the mixtures of glycols or PEGs with the two aryl alcohols studied previously [9,10]. Furthermore, in the series PA, PEAL and PPAL ($n = 1, 2, 3$, respectively), the H_m^E of PPG is always larger

Table 3
Least-squares parameters, a_k, Eq. (1) and standard deviations

Mixture	a_0	a_1	a_2	a_3	a_4	a_5	$\sigma(H_m^E)$
EG + PPAL	1251.550	−189.4659	913.9834	−306.4066	70.2868	331.7032	1.52
PPG + PPAL	1384.920	−137.6937	957.6626	35.7316	225.7114		2.92
DEG + PPAL	−739.5337	160.7371	−1088.6722	281.8711			1.50
TEG + PPAL	−345.3637	62.1996	−467.5279	287.5232			0.75
TETG + PPAL	−691.2666	112.2028	−167.7326	616.2758	−1073.6389		1.37
PEG200 + PPAL	−641.2606	−0.6935	−111.2610	677.7263	−1017.5352		1.20
PEG300 + PPAL	−666.8770	223.7025	128.0572	741.2832	−1302.6547		1.46
PEG400 + PPAL	−695.1724	412.6063	184.5037	548.9847	−1220.1914	154.3024	1.42
PEG600 + PPAL	−751.6679	586.6583	763.3076	488.7509	−2213.6820	117.7578	1.20

$\sigma(H_m^E)$ of binary mixtures containing: ethylene glycol or propylene glycol or di(ethylene glycol) or tri(ethylene glycol) or tetra(ethylene glycol) (TETG) or PEG200 or PEG300 or PEG400 or PEG600 (component 1) + 3-phenylpropyl alcohol (component 2) at 308.15 K.

than the one of EG, due to the hindrance of the CH_3 group in the secondary OH of PPG. This effect has been just observed by us in a previous work, dealing with the mixtures of glycols or PEGs with dimethyl sulfoxide [8]. However, a comparison of the H_m^E's of mixtures of homologous alcohols with EG or PPG ($p = 0$) shows some differences. For $n = 1$ and $n = 2$, the H_m^E's are nearly the same, whereas for $n = 3$, H_m^E results larger of about 50%. If we assume that $H_m^E \propto E_{11} + E_{22} - 2E_{12}$, with E_{ij} the interaction energy between molecules 1 and 2, then the term $E_{22} - 2E_{12}$ can be considered nearly the same passing from BA to PEAL. The larger is OH···OH bond strength for self-association of alcohols, the larger is the OH···OH interaction between alcohols and EG, thus H_m^E depends largely on E_{11} and we observe positive values of the enthalpy of mixing. On the contrary, for PPAL, we must assume that the introduction of a third CH_2 group in the aliphatic chain of alcohol decreases drastically the strength of the interactions E_{12} between the different molecules of the mixtures, leading to the larger values of H_m^E.

Also, in the case of $p > 0$, the comparison of the H_m^E data of Fig. 1, referring to PPAL, with the corresponding H_m^E obtained for BA [9] and PEAL [10], shows the effects of both the increase of the molecular weight of glycols or PEGs and the increase of the length of alkyl chain of the alcohol. Particularly, the decrease of H_m^E with the increasing molecular weight of glycols or PEGs in the mixtures with PPAL follows, as said, the same trend observed for the other alcohols ($n = 1$ and $n = 2$) and may be explained with the increase of the number p of the H-bond acceptors ethereal units OP with the consequent increase of the intermolecular hydrogen bonding energy E_{12}. However, the curves H_m^E versus x_1, for DEG, TEG and TETG with PPAL show marked low values for DEG, in contrast with the corresponding curves for BA and PEAL, where the sequence DEG > TEG > TETG is respected. This anomalous behavior may find a qualitative interpretation considering that PPAL and DEG have similar length of the side alkyl and CH_2–O–CH_2 chains, in alcohol and DEG, respectively. As a consequence, the two molecules can approach better each to the other with a stronger hydrogen bonding between the OH groups, with eventual formation of a ring.

Referring to the role of the different alcohols present in the mixtures, really, the minima of H_m^E of PEG 600 ($p = 11.17$), for instance, are −1200, −600, and $-200\,\mathrm{J\,mol^{-1}}$, in passing from $n = 1$ to $n = 3$, with negative values of H_m^E indicating strong interactions between the molecules of components 1 and 2. However, these interactions markedly decrease with the increase of the molecular dimension of alcohols due to a progressive lack of involvement of the ethereal groups of glycols or PEGs to the H-bonding.

Finally, Fig. 1 shows, for PPAL, the same intersection of curves obtained for the other alcohols ($n = 1$ and $n = 2$).

In the glycol-rich region, the curves H_m^E versus x_1, for PEGs, show a thermal effect with a molecular weight dependence in an inverted order with respect to the one given in the glycol poor region. This behavior probably results from a variation in the chain conformation of polymer, which was observed in aqueous solutions [16].

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