A calorimetric study of binary mixtures containing some glycols and polyglycols + anisole at 308.15 K and at atmospheric pressure

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Abstract

Excess molar enthalpies, H_m^E, of binary mixtures of anisole + glycols and polyglycols were measured by a flow microcalorimeter at 308.15 K and at atmospheric pressure over the whole composition range. Binary mixtures contained anisole + diethylene glycol, anisole + triethylene glycol, anisole + tetraethylene glycol, anisole + poly(ethylene glycol)-200, anisole + poly(ethylene glycol)-300, anisole + poly(ethylene glycol)-400, anisole + poly(ethylene glycol)-600. Effects of the molecular weight distribution (MWD), of the polymer were investigated too, by preparing three additional samples of poly(ethylene glycol) (PEG) with the same number average molecular weight ($M_n \approx 300$), but different MWD. Values of H_m^E of the corresponding binary mixtures with anisole were measured. For all mixtures, results were fitted to the Redlich–Kister polynomial. H_m^E curves are asymmetrical, showing positive deviations for mixtures containing glycols and poly(ethylene glycol)-200, negative deviations for poly(ethylene glycol)-600, and an inversion of sign in the other cases. Values of H_m^E vary from a maximum of 440 J mol^{-1} (anisole + triethylene glycol) to a minimum of -390 J mol^{-1} (anisole + poly(ethylene glycol)-600). Effects of changes in the glycols chain length and in MWD on the molecular interactions between the mixture components are discussed.
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1. Introduction

Poly(ethylene glycol) (PEG) encompasses a series of linear oligomers/polymers of oxyethylene units, terminated by hydroxyl groups at both chain-ends. Their low toxicity and non-irritating nature led to a wide range of applications in the pharmaceutical,

petroleum, cosmetic and food industry [1]. Moreover, solubility of PEG in both water and in a large number of organic solvents is a valuable property in the development of environmental friendly processes, like the design of water soluble catalyst, and the purification of biological substances [2–4]. Chemical and physical properties of PEG are strongly affected by the length of the polymer chain. The monomeric unit embodies a hydrophobic region ($-CH_2-CH_2-$) and a hydrogen bonding site ($-O-$), whereas end-groups are strongly hydrophilic. Shorter chains bear a more

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distinct glycolic character, since the relative contribution of the hydroxyl end-groups is significant, especially for solubility [5] and miscibility in blends [6]. End-group effects become less important as molecular weight is increased. This change in properties is also reflected in the nomenclature, where the term poly(ethylene oxide) (PEO) is preferentially used for high molecular weight PEG (>10 000 Da). At room temperature, low molecular weight PEGs are viscous fluids, changing into glassy polymers and hard crystalline solids as the molecular weight is increased. In the crystals, PEG molecules take a 7_2 helical structure (seven monomeric units for two turns of the helix) [7] with an identity period of 2.0 nm [8]. Molecular mass of the polymer seems to control its conformation in aqueous solution. PEG of high molecular mass retains its helical structure, with the hydrocarbon groups inside the helix, whereas low molecular mass PEG displays random coil conformation [9].

Solution properties of binary mixtures of PEG with some monoethers and diethers have been previously investigated. Excess molar volumes, viscosity deviations and excess molar enthalpies, H_m^E, have been reported for solutions of PEG with linear diethers (dimethoxymethane and 1,2-dimethoxyethane) [10], cyclic monoethers (oxolane and oxane) [11,12] and cyclic diethers (1,3-dioxolane and 1,4-dioxane) [11]. Properties of these mixtures are strongly dependent on changes in both the molecular structure of the ethers and the number of etheric O-atoms. These correlations have been qualitatively explained in terms of perturbation of the PEG H-bond network by addition of the ether component. In keeping with this research program, in the present work, we selected anisole (methoxybenzene) to investigate excess molar enthalpies of binary mixtures with a series of glycols and polyglycols.

Anisole is a solvent widely used in the perfume industry and in organic syntheses. It displays a dipole moment μ, of 1.2 D and a relative permittivity ε, of 4.33 at 298.15 K. The –O–CH$_3$ group of anisole can give some degrees of intermolecular association by weak H-bonds [13]. In contrast, glycols display relatively low values of dipole moment and relative permittivity and their hydroxyl end groups provide strong H-bonds. Thus, in the liquid state, glycols and PEGs can develop a relatively extended network of intermolecular H-bonds. Thermodynamic properties, as

excess molar enthalpies, H_m^E, of mixtures containing anisole+glycols and PEGs can prove useful to investigate competition between homomolecular and heteromolecular interactions. It is also of interest to evaluate the effect of the large aromatic ring of anisole on interaction properties, and to draw comparisons with binary mixtures of linear and cyclic ethers and diethers.

Thus, in this paper, we report the excess molar enthalpies, H_m^E, of diethylene glycol (DG), triethylene glycol (TG), tetraethylene glycol (TEG), PEG-200, PEG-300, PEG-400, and PEG-600 + anisole (A) at 308.15 K and at atmospheric pressure. Moreover, effects of molecular mass distribution have been investigated by measuring values of H_m^E for three additional binary systems containing mixtures of PEGs having the same number average molecular weight ($M_n \approx$ 300), but different values of the corresponding weight average molecular weight, M_w. To our knowledge, no enthalpy data are reported in the literature for these systems.

2. Experimental

2.1. Chemicals

Chemicals were purchased from Fluka and Aldrich and used without further purification. The molecular weights of PEG were measured by gel permeation chromatography (GPC), whereas their purity was ascertained by electrospray (ESI) mass spectrometric analysis [11]. The number average, M_n $\left(= \sum N_i M_i / \sum N_i \right)$, and the weight average, M_w $\left(= \sum N_i M_i^2 / \sum N_i M_i = \sum w_i M_i \right)$, 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. Three additional samples of PEG were prepared by mixing PEG-300 with PEG-400 (mix1), PEG-200 with PEG-400 (mix2) and PEG-200 with PEG-600 (mix3). The relative amounts of the two components were adjusted to provide mixtures with the same number average molecular weight ($M_n \approx 300$), but different values of the polydispersity index. Also for these three additional samples, values of M_n and M_w were measured by GPC. Table 1 reports molecular weights and polydispersity index of the PEG samples.

Table 1
Purities, sources, and densities, ρ, of pure components at 308.15 K and comparison with literature data

Component	Source	M_w	M_w/M_n	ρ (g cm^{-3})	
				Experiment	Literature
DG (99%)	Aldrich			1.10565	1.10557 [14]
TG (99%)	Aldrich			1.11209	1.11209 [14]
TEG (99%)	Aldrich			1.11228	1.1128 [15]
					1.11228 [16]
PEG-200	Fluka	204	1.11	1.11284	1.11243 [14]
PEG-300	Fluka	305	1.11	1.11358	1.11328 [14]
PEG-400	Fluka	401	1.10	1.11489	1.11372 [16]
PEG-600	Fluka	588	1.06	1.11396	
Mix1 (PEG-300 + PEG-400)		340	1.15	1.11398	
Mix2 (PEG-200 + PEG-400)		361	1.22	1.11393	
Mix3 (PEG-200 + PEG-600)		437	1.51	1.11386	
Anisole (99%)	Aldrich			0.97978	0.9798 [17]

The purities of the chemicals were checked by comparing the measured densities ρ, with those reported in the literature [14–17]. Densities were determined by a vibrating tube density meter (Anton Paar, model 60, Graz, Austria), equipped with a measuring cell (type 602) operated in the static mode. The cell is thermostated by a circulating water bath (Heto, type DTB 623, Denmark) with a precision of ±0.01 K. The operating procedure of the apparatus was described previously [18]. Uncertainty in density, determined at atmospheric pressure, is estimated to be ±1 × 10^{-5} g cm^{-3}. Table 1 reports purities, sources and densities of mixture components at 308.15 K, compared to literature data [14–17]. Before measurements, anisole, DG, TG and TEG were degassed by ultrasound (ultrasonic bath, Hellma, type 460, Milan, Italy), dried over molecular sieves (Union Carbide, type 4A, 1/16 in. pellets) and stored in dark bottles.

2.2. Calorimetric measurements

Excess molar enthalpies were measured by a flow microcalorimeter (LKB Producer AB, model 2107, Bromma, Sweden) equipped with a digital unit for data acquisition, and two automatic burettes (ABU, Radiometer, Copenhagen), to pump pure liquids into the mixing cell. The heat sink of the microcalorimeter contains the reference and the mixing cells and its temperature is controlled by a thermostatic water bath with a precision of ±0.01 K. Details of the apparatus and operating procedure were described elsewhere [19,20]. Mole fractions, x_1, of glycols and PEGs were

computed from molecular weights, densities, and volumetric flow rates of components 1 and 2, as stated by the automatic burettes. Flow rates were selected to cover the entire mole fraction range. The performance and reliability of the microcalorimeter 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 literature data [21].

3. Correlation of the calorimetric data

The experimental values of the H_m^E of mixing for the binary mixtures reported in this paper are listed in Table 2 and plotted in Figs. 1–3. For each binary mixture, a Redlich–Kister polynomial [22] of the type

$$H_m^E = x_1 x_2 \sum_{k \geq 2} a_k (x_1 - x_2)^k \tag{1}$$

has been fitted to experimental values by a method of unweighted least-squares. In Eq. (1), x_1 and x_2 are the molar fractions of components 1 and 2, respectively, and $a_k s$ are adjustable parameters. Values of a_k are reported in Table 3, together with the standard deviation $\sigma(H_m^E)$ defined as

$$\sigma(H_m^E) = \left| \frac{\phi_{min}}{N - n} \right|^{0.5} \tag{2}$$

where N and n are the number of experimental points and of adjustable parameters, respectively. ϕ_{min} is

Table 2
Excess molar enthalpies, H_m^E, of binary mixtures at 308.15 K[a]

x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})
Diethylene glycol + anisole			
0.0417	189.1	0.5349	191.4
0.0457	202.0	0.6331	147.1
0.0874	300.1	0.6970	121.4
0.1257	337.4	0.7753	80.0
0.1608	344.6	0.8214	58.1
0.2233	328.1	0.8734	35.2
0.2771	303.1	0.9020	25.3
0.3651	255.0	0.9324	16.5
0.4339	226.7	0.9650	7.9
Triethylene glycol + anisole			
0.9519	37.4	0.3547	388.8
0.9082	62.9	0.2920	408.3
0.8684	84.2	0.2156	433.7
0.8319	106.4	0.1709	437.0
0.7674	153.7	0.1208	413.0
0.7122	194.7	0.0935	379.0
0.6226	265.1	0.0643	307.8
0.5531	307.2	0.0332	191.8
0.4520	361.2	0.0303	178.0
Tetraethylene glycol + anisole			
0.0257	77.4	0.4868	153.8
0.0500	127.2	0.5583	125.8
0.0732	163.3	0.6547	85.2
0.0953	192.9	0.7166	55.3
0.1365	222.8	0.7914	27.2
0.1740	227.8	0.8349	15.5
0.2401	222.4	0.8835	4.1
0.2964	207.0	0.9382	2.2
0.3873	189.0		
PEG-200 + anisole			
0.0260	116.5	0.4898	179.8
0.0506	193.6	0.5613	151.6
0.0740	243.1	0.6574	97.7
0.0963	273.5	0.7190	66.0
0.1379	298.5	0.7933	29.1
0.1758	298.9	0.8365	15.4
0.2423	275.4	0.8848	8.1
0.2989	253.6	0.9389	4.3
0.3901	222.5		
PEG-300 + anisole			
0.0140	40.6	0.4023	32.7
0.0183	51.1	0.4729	11.1
0.0360	87.3	0.5737	−32.6
0.0531	111.1	0.6421	−63.0
0.1695	128.8	0.7291	−84.9
0.1008	141.6	0.7821	−91.1
0.1301	141.6	0.8433	−82.8
0.1832	120.5	0.9150	−44.9
0.2301	97.6	0.9349	−29.4
0.3097	59.3		

Table 2 (*Continued*)

| x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})
PEG-400 + anisole			
0.0104	18.7	0.3358	−149.3
0.0138	23.9	0.4025	−174.7
0.0273	40.0	0.5027	−200.0
0.0404	49.9	0.5740	−215.1
0.0532	53.1	0.6691	−223.9
0.0777	52.8	0.7294	−216.1
0.1009	40.4	0.8017	−185.7
0.1442	4.5	0.8899	−107.2
0.1833	−34.2	0.9151	−79.5
0.2520	−95.0		
PEG-600 + anisole			
0.0182	−33.9	0.3074	−304.2
0.0270	−49.1	0.3997	−357.4
0.0357	−63.2	0.4703	−385.7
0.0526	−88.3	0.5711	−386.8
0.0689	−112.0	0.6397	−369.5
0.0999	−148.3	0.7270	−311.6
0.1288	−180.2	0.8419	−191.2
0.1816	−230.3	0.9244	−86.0
0.2498	−272.4		
Mix1 (PEG-300 + PEG-400) + anisole			
0.0452	50.8	0.6305	−36.0
0.0865	84.8	0.6946	−50.1
0.1244	107.5	0.7733	−75.6
0.1593	121.5	0.8198	−97.1
0.2213	127.1	0.8722	−117.0
0.2748	120.2	0.9009	−116.0
0.3624	86.6	0.9317	−93.9
0.4311	49.8	0.9647	−42.0
0.5320	−2.5	0.9733	−26.1
Mix2 (PEG-200 + PEG-400) + anisole			
0.0452	48.9	0.6305	−39.2
0.0865	81.4	0.6945	−51.9
0.1244	103.2	0.7733	−75.3
0.1573	115.5	0.8197	−96.0
0.2213	122.6	0.8722	−115.7
0.2748	114.2	0.9009	−116.3
0.3678	80.0	0.9317	−99.6
0.4311	46.1	0.9647	−51.4
0.5320	−5.8	0.9732	−36.3
Mix3 (PEG-200 + PEG-600) + anisole			
0.0452	44.6	0.6304	−41.9
0.0865	73.9	0.6945	−58.2
0.1244	92.6	0.7733	−87.2
0.1593	102.0	0.8197	−109.8
0.2213	108.1	0.8722	−128.3
0.2748	100.2	0.9009	−126.0
0.3624	69.0	0.9317	−105.0
0.4310	37.9	0.9646	−54.0
0.5320	−8.5	0.9732	−37.0

[a] Glycols and polyglycols are labeled as component 1.
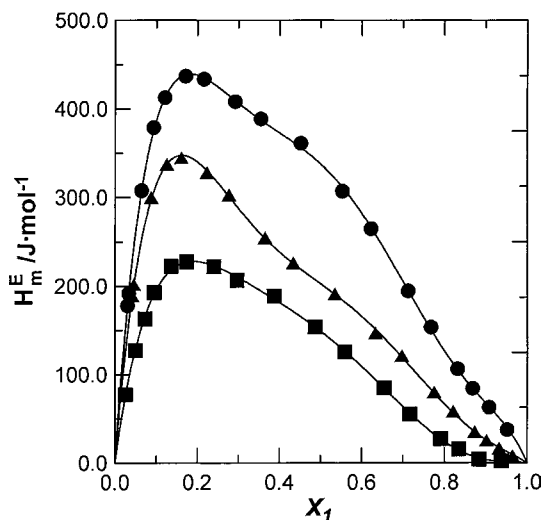
Fig. 1. Excess molar enthalpies, H_m^E, for binary mixtures of glycols(1) + anisole(2) at 308.15 K: (▲), (●), and (■) refer to mixtures containing DG, TG, and TEG, respectively; solid curves, Redlich–Kister equation.

the minimum value of the objective function ϕ defined as

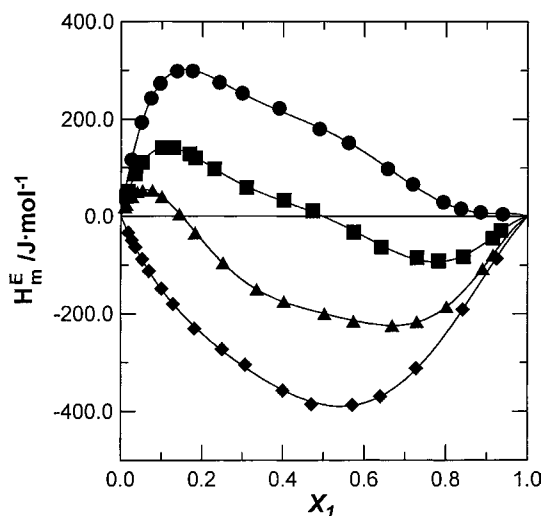$$\phi = \sum_{k=1}^{N} \xi_k^2 \tag{3}$$

Fig. 2. Excess molar enthalpies, H_m^E, for binary mixtures of PEGs(1)+anisole(2) at 308.15 K: (●), (■), (▲), and (◆) refer to mixtures containing PEG-200, PEG-300, PEG-400, and PEG-600, respectively; solid curves, Redlich–Kister equation.
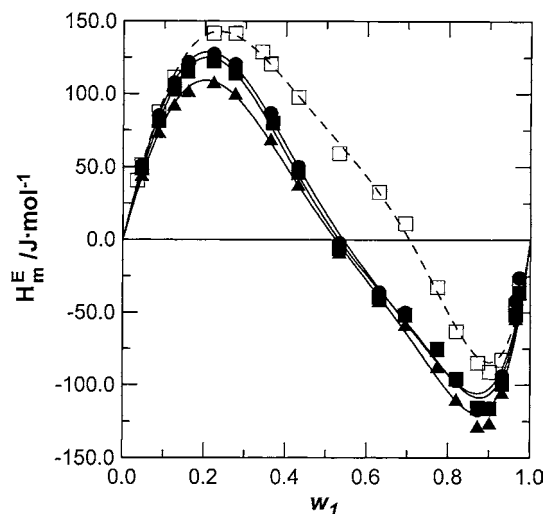

Fig. 3. Excess molar enthalpies, H_m^E, for binary mixtures of mixtures of PEGs(1) + anisole(2) at 308.15 K: (●), (■), and (▲) refer to mixture mix1 (PEGs-300 + PEGs-400), mix2 (PEGs-200 + PEGs-400), and mix3 (PEGs-200 + PEGs-600), respectively; (□) refers to mixture containing PEG-300 as comparison; solid and dashed lines, Redlich–Kister equation.

where $\xi_k = H_{m,calcd}^E - H_m^E$; H_m^E is the experimental value and $H_{m,calcd}^E$ is evaluated by Eq. (1).

4. Results and discussion

Table 2 reports the experimental values of H_m^E for the mixtures investigated in this work. Excess molar enthalpies for binary mixtures of anisole and monomeric glycols are plotted in Fig. 1 vs. the glycol molar fraction. Values of H_m^E are positive in the whole mole fraction range, increasing, as the glycol is changed, along the sequence tetraethylene glycol < diethylene glycol < triethylene glycol. Plots reported in Fig. 2 show that, for binary mixtures of PEG-200 + anisole, H_m^E values are still positive in the whole mole fraction range. However, H_m^E decreases as M_w of the polymer is increased. For PEG-300 and PEG-400, plots of H_m^E display an inversion of sign and H_m^E becomes negative as the molar fraction of PEG is increased. For PEG-600 (the highest M_w studied in this work) H_m^E is negative in the whole range of x_1 (Fig. 2).

Fig. 3 reports the plots obtained from mixtures of two different PEG samples + anisole. Molecular

Table 3
Least-squares parameters, a_k, Eq. (1), and standard deviations, $\sigma(H_m^E)$, Eq. (3), for experimental excess molar enthalpies, H_m^E, of binary mixtures containing glycols and poly(ethylene glycols) (component 1) + anisole (component 2) at 308.15 K

Component 1	a_0	a_1	a_2	a_3	a_4	$\sigma(H_m^E)$ (J mol^{-1})
DG	811.82	−677.71	730.81	−2073.2	1508.7	2.0
TG	1350.9	−858.92	269.67	−2120.2	2445.7	2.5
TEG	596.82	−715.80	185.45	−965.19	960.60	2.4
PEG-200	715.07	−784.94	84.612	−1701.6	1968.5	2.2
PEG-300	−3.0803	−713.70	−542.54	−985.81	2057.5	2.2
PEG-400	−797.02	−414.29	−609.80	−841.30	2155.6	0.9
PEG-600	−1544.6	−311.24	113.73	849.40		2.9
Mix1 (PEG-300 + PEG-400)	−244.19	−468.91	−713.36	−1176.8	2779.2	0.6
Mix2 (PEG-200 + PEG-400)	−248.50	−422.26	−656.87	−1298.4	2497.4	0.7
Mix3 (PEG 200 + PEG-600)	−278.02	−533.42	−660.81	−1004.4	2335.3	0.7

weights of the PEG mixtures are the same ($M_n \approx 300$), but the polidispersity index is higher especially for mix2 and mix3, as compared to the previous PEG samples. Thus, to avoid problems related to the evaluation of the molar fraction for these compounds, H_m^E values have been plotted vs. the mass fraction, w_1. The dashed curve in Fig. 3 refers to PEG-300+anisole and is reported for comparison. Plots in Fig. 3 show that values of H_m^E for the three PEG mixtures are similar, with an inversion of sign as w_1 ranges from 0 to 1. Lower values of H_m^E are obtained for the binary mixture containing mix3 (PEG-200+PEG-600), while curves of mix1 (PEG-200+PEG-400) and mix2 (PEG-300 + PEG-400) are almost superimposed. A comparison with data of PEG-300 + anisole (Fig. 3, dashed line) shows that for this mixture the inversion of sign is shifted to larger values of w_1.

5. Conclusions

Data in Figs. 1–3 show that H_m^E depends strongly on both the molecular weight and the polydispersity of glycols. With the exception of the binary mixture of diethylene glycol + anisole, H_m^E decreases as the glycol molecular weight is increased. Trends reported in these figures can be qualitatively explained by assuming that $H_m^E \propto E_{11} + E_{22} - 2E_{12}$, where E_{ij} is the interaction energy between molecules of type i and j. From this relationship, positive values of H_m^E correspond to $E_{11} + E_{22} > 2E_{12}$, implying that homomolecular interactions are stronger than heteromolecular interactions, between glycols and anisole.

According to Figs. 1 and 2, this conclusion holds for monomeric glycols and PEG-200. However, as glycol molecular weight increases further, H_m^E displays negative values in wider and wider composition intervals ($2E_{12} > E_{11} + E_{22}$), where homomolecular interactions become correspondingly weaker. Moreover, the interaction energy between anisole molecules, E_{22}, is constant, because, for this component, the same grade is used throughout all mixtures. Thus, for a given composition, changes in H_m^E of different mixtures should be determined only by the value of $E_{11} - 2E_{12}$. The decrease of H_m^E as M_w of the glycols is increased may correspond either to a decrease in E_{11} or increases in E_{12} or both. E_{11} can be estimated by the heat of vaporization [23], ΔH_{vap}, and a survey of literature data shows that ΔH_{vap} is 65.6 kJ/mol for monoethylene glycol [24], 62.0 for DG [25] and 59.5 for TG [25]. These data are consistent with a decrease of E_{11} as M_w is increased, at least for low M_w, but are in contrast with the trends in Fig. 1 for the mixtures with DG and TG. Moreover, more complete sets of data on similar compounds, the ω-alkanediols, show an increase in ΔH_{vap} as the number of methylene groups in the chain is increased [24].

The anomalous lower H_m^E values of DG mixtures as compared to TG must be attributed to the E_{12} term. Actually, according to the above reported values of ΔH_{vap} (62.0 vs. 59.5 kJ/mol), E_{11} should be larger for DG mixtures. Thus, the decrease in H_m^E, reported in Fig. 1, must stem from E_{12} significantly larger than the corresponding values for the TG mixture. This anomalous trend is likely attributable to the fact that DG is the only substance in the set of glycols investigated

in this work, which has a single etheric O-atom in the chain. In fact, the available conformational set for DG cannot enclose *cis*-conformations of two subsequent etheric O-atoms that lead to more packed molecular arrangement in solution, likely less favorable to the development of strong anisole–glycol interactions.

Contributions to molecular interactions stem mainly from three types of forces: dispersion forces, polar forces and hydrogen bonding. For glycols, increases in the chain length provide more flexible chains by addition of etheric O-atoms, as well as a decrease of strong H-bonds between the OH end-groups and an increase in weak [13] H-bonds O–H $\cdots$ CH$_2$. The conformation of the PEG chains in the mixture is likely the crucial parameter, which determines the relative influence of the above-mentioned effects on the molecular interaction forces. Actually, for PEGs of high M_w, the helical conformations can keep hydrophobic groups inside the helix, whereas the coils, typical of low M_w chains, display a random arrangement of groups [9]. Thus, E_{12} should increase as the length of PEG chains is increased. Actually, head-to-tail interactions between OH terminal groups become less effective, while, for each PEG molecule, larger numbers of etheric O-atoms become available to interact with anisole molecules. Trends reported in Figs. 1 and 2 are consistent with this model. Moreover, Fig. 2 shows that for $M_w \geq 300$ increases in E_{12} are so important that increasing portions of H_m^E values become negative. For M_w close to 300, this effect is confined to the PEG-rich portion of the plot, but it extends towards lower values of x_1 as M_w is increased. For $M_w \approx 600$, H_m^E is negative in the whole composition interval. These data lead to conclude that for $M_w \approx 300$ PEG–PEG interactions are weak and additions of small amounts of anisole can provide significant increases in E_{12}. For $x_1 < 0.5$ the E_{22} term is large enough to keep H_m^E above 0. However, as M_w is further increased, heteromolecular interactions become so significant to dominate the whole range of compositions.

It is of interest to compare H_m^E of PEG-200 and TEG, since the molecular weight of this compound is 194, viz. close to the M_w of PEG-200 (Table 1). As reported in Table 2, the maximum values of H_m^E for the mixtures of these compounds occur at the same composition ($x_1 \approx 0.17$), but H_m^E of PEG-200 is 70 J mol^{-1} larger. TEG is a monodisperse sample, viz. its molecules are of the same size. In contrast PEG-200

is synthesized as a polymer with a polidispersity index of 1.17 (Table 1) and, according to the trends reported in Figs. 1 and 2, the contribution of the shorter chains should increase H_m^E above the corresponding values of TEG. Effects of the molecular weight distribution (MWD) are more evident in the data reported in Fig. 3. In fact, the average molecular weights of all samples in this figure are quite close. However, as compared to PEG-300 (Fig. 3, dashed line), H_m^E values of mix1, mix2 and mix3 are lower than expected and the corresponding plots are consistently shifted to the right, a behavior that is typical of samples of higher M_w. These trends can be attributed to the high molecular weight tails of the PEG-400 and PEG-600 fractions in these samples. The contribution of heterogeneous molecular interaction energy, E_{12}, becomes more important by the larger number of helical conformations and the weakening of head-to-tail interactions as the length of the PEG chain is increased. This conclusion is also consistent with the lower values of H_m^E for the binary mixture containing mix3 (PEG $200 + 600$), that is the mixture with the highest molecular weight fraction of PEG.

A final remark can be made on data reported in Table 1. Densities of different PEG samples display only slight changes with M_w and polidispersity. In contrast, these molecular parameters have a major influence on the thermodynamic properties of PEG solutions. This may prove a useful property in industrial applications and in the design of particular synthetic routes involving PEGs.

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