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Excess molar enthalpies of binary mixtures containing ethylene glycols or poly(ethylene glycols) + ethyl alcohol at 308.15 K and atmospheric pressure

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Abstract

Excess molar enthalpies, H_m^E, of binary mixtures containing ethylene glycols and poly(glycols) + ethyl alcohol were measured by a flow microcalorimeter at 308.15 K and at atmospheric pressure over the whole composition range. Binary mixtures contain ethyl alcohol + ethylene glycol, + di(ethylene glycol), + tri(ethylene glycol), + tetra(ethylene glycol), + poly(ethylene glycol)-200, + poly(ethylene glycol)-300, + poly(ethylene glycol)-400, + 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) with the same number average molecular weight ($M_n \approx 300$), but different MWD. For all mixtures, results were fitted to the Redlich–Kister polynomial. H_m^E curves are asymmetrical, showing positive values which vary from 280 J mol^{-1} (diethylene glycol + ethyl alcohol) to 1034 J mol^{-1} (mixture containing PEGs (200 + 400) + ethyl alcohol). Effects of changes in the glycols chain length and in MWD on the molecular interactions among the mixture components are discussed.

Keywords: Excess molar enthalpy; Poly(ethylene glycol); Calorimeter; Correlation data

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1. Introduction

In recent years, numerous studies have been carried out on mixtures containing poly(ethylene glycols) (PEGs). PEG is a linear polymer of oxyethylene units with hydroxyl groups at both chain-ends. Poly(ethylene glycol) has numerous uses in biotechnology [1,2], in chemical partitioning [3–5], and most recently in extractive crystallization of inorganic salts [6]. Actually, the low toxicity of PEGs has favoured its usage in the pharmaceutical, cosmetic and texile fields [7,8], and as additive in the production of films for food coating [9].

The monomeric unit embodies a hydrophobic region ($-CH_2-CH_2-$) and a H-bonding site ($-O-$), whereas end-groups are strongly hydrophilic. For shorter chains the hydroxyl end-groups contribute significantly to the physical and chemical properties of PEGs, especially solubility [10] and miscibility in blends [11], but their importance decreases as chain length is increased. At room temperature, low molecular weight PEGs are viscous fluids or waxy solids, while larger molecular weights correspond to glassy polymers and hard crystalline solids. In the crystal, PEG chains are arranged in 7_2 helical structure (seven monomeric units for two turns of the helix) [12] with an identity period of 2.0 nm [13]. In aqueous solutions PEG chain conformation seems to depend on the molecular mass: PEG of large molecular mass retains its helical structure, with the hydrophobic methylene groups inside the helix, whereas low molecular mass PEG displays random coil conformation [14].

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In the present paper, excess molar enthalpies, H_m^E, have been measured for binary mixtures containing ethylene glycol (EG), di(ethylene glycol) (DEG), tri(ethylene glycol) (TEG), tetra(ethylene glycol) (TETG), PEG-200, PEG-300, PEG-400, PEG-600, mix1 (PEG-300 + PEG-400), mix2 (PEG-200 + PEG-400), and mix3 (PEG-200 + PEG-600) + ethyl alcohol (EtOH).

PEG hydroxyl end groups can interact via strong H-bonds, developing relatively extended networks of associated molecules. Additional interactions stem from weak H-bonds between methylenes and the O-atoms of the oxymethylene units [15]. Interactions with the alcoholic groups of ethyl alcohol can perturb this H-bond network.

Some PEGs samples used in this work are mixtures of two polymers with narrow molecular mass distribution (MMD). The final samples display similar number average molar masses but different MMD. Actually, the main purpose of the present work is to investigate MMD effects on the excess molar enthalpies, H_m^E, of binary mixtures with ethyl alcohol and to correlate these effects with the type and strength of molecular interactions. For a given set of different PEG grades it is possible to modify the MMD of PEG samples by mixing grades in different proportions. Samples can be prepared with pre-selected values of the different moments of the MMD, such as number or weight average molecular masses. No data have been found in the literature on binary mixtures studied in this paper.

2. Experimental

2.1. Materials

Glycols were purchased from Aldrich while PEGs from Fluka, analytical grade ≥99% and were used without further purification. PEG-200, PEG-300, PEG-400, and PEG-600 were used to prepare three polymeric mixtures, as described later. Ethyl alcohol was from Merck, analytical grade 99.9%. Purities of the products were checked on a Hewlett-Packard gas chromatograph model 5890 by using an HP (cross-linked 5% ME siloxane) capillary column and the stated purities were confirmed. Before measurements chemicals were degassed by ultrasound (ultrasonic bath, type 400, Hellma, Milan, Italy), kept in dark bottles, and dried over molecular sieves (Union Carbide, type 4A, 1/16 in. pellets).

2.2. GPC analysis

A PL-GPC 110 (Polymer Laboratories) thermostated system, equipped with three PL-gel 5 μm columns (two mixed-D and one mixed-E) attached in series, was used. The analyses were performed at $35 \pm 0.1\,^{\circ}\mathrm{C}$ using THF as eluant at a flow rate of 1 mL/min. A differential refractometer (Polymer Laboratories) was used as detector. The instrument was calibrated with a mixture of seven PEG standards (Polymer Laboratories; molecular masses between 64 and 1450 Da) using the PL-caliber GPC software for the determination of the average molecular masses and polydispersity of the polymer samples.

2.3. Sample preparation

PEG-200, PEG-300, PEG-400, and PEG-600 were analyzed by GPC and the number average, M_n ($= \sum N_i M_i / \sum N_i$), and the weight average, M_w ($= \sum N_i M_i^2 / \sum N_i M_i = \sum w_i M_i$), molecular weights were determined. In the above equalities, N_i is the number of moles of species i, having molecular mass M_i, and weight fraction w_i. A polydispersity index was obtained as the ratio M_w/M_n. For PEG-200 M_n was equal to 192 and M_w/M_n to 1.16, for PEG-300 $M_n = 274$ ($M_w/M_n = 1.11$), for PEG-400 $M_n = 365$ ($M_w/M_n = 1.10$), and for PEG-600 $M_n = 554$ ($M_w/M_n = 1.060$).

To obtain PEG mixtures of similar M_n (≈300) but different MMD, suitable amounts of these grades were mixed and maintained at 50 °C under magnetic stirring for 30 min. The average molecular masses of these polymeric mixtures were subsequently determined by GPC and the component amounts in each mixture were adjusted to obtain four samples: mix1 (PEG-300, 600 g + PEG-400, 270 g), mix2 (PEG-200, 300 g + PEG-400, 700 g), and mix3 (PEG-200, 550 g + PEG-600, 550 g). Table 1 reports values of M_n, and M_w/M_n for these polymeric mixtures.

2.4. MALDI-TOF mass spectrometric analysis

To ascertain the purity of PEGs used in this work, MALDI-TOF mass spectrometric analysis (by using a Voyager DE-STR instrument from PerSeptive Biosystem) was undertaken using *trans*-3-indoleacrylic acid as a matrix. In the spectra (omitted for brevity), only peaks corresponding to molecules of PEG di-hydroxy terminated $H{-}[O{-}CH_2{-}CH_2]_n{-}OH$ cationized with Na^+ and K^+, together with traces of PEG molecules cationized with H^+, are present. No peaks due to impurities are detected, so that the samples can be considered substantially pure.

2.5. Calorimetric measurements

The excess enthalpies, H_m^E, were measured by a flow isothermal calorimeter (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 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. The pure components are pumped into the mixing cell at selected flow rates. The component mole fractions in the mixed stream were calculated from densities and volumetric flow rates of components 1 (Glycols or PEGs) and 2 (ethyl alcohol). The total flow rates are usually kept at about $0.4\,\mathrm{cm^3\,min^{-1}}$, but, in dilute regions, the total flow rates may increase up to $0.8\,\mathrm{cm^3\,min^{-1}}$. Details

Table 1
Number average, M_n, M_w/M_n, and densities, ρ, of pure components at 308.15 K and comparison with literature data

Component	M_n	M_w/M_n	ρ (g cm^{-3})	
			Experimental	Literature
Ethylene glycol	62.07		1.10293	1.10294 [19]
Di(ethylene glycol)	106.12		1.10565	1.10557 [20]
Tri(ethylene glycol)	150.17		1.11209	1.11209 [20]
Tetra(ethylene glycol)	194.23		1.11228	1.11228[19]
PEG-200	192	1.16	1.11284	1.11243 [20]
PEG-300	274	1.11	1.11358	1.11328 [20]
PEG-400	365	1.10	1.11413	1.11372 [19]
PEG-600	554	1.06	1.11396	
Mix1 (PEG-300 + PEG-400)	296	1.15	1.11398	
Mix2 (PEG-200 + PEG-400)	295	1.22	1.11393	
Mix3 (PEG-200 + PEG-600)	290	1.51	1.11386	
Ethyl alcohol	46.07		0.77641	0.77641 [21]

and operating procedure of the apparatus have been reported elsewhere [16,17]. The accuracy of the reported H_m^E values in this study was verified by measurements on three standard systems, cyclohexane + hexane, benzene + cyclohexane, and methanol + water at 298.15 K that are known in the literature [18]. Agreement with literature data was better than 0.5% at the maximum of the thermal effect. Uncertainties in H_m^E and in molar fractions x_1 of ethylene glycols and PEGs are estimated to be less than 1% and 2×10^{-4}, respectively.

Densities, ρ, of pure compounds were measured using a vibrating tube density meter (Anton Paar, model DMA 60/602, Graz, Austria), thermostated at (308.15 ± 0.01) K by a circulating external bath (Heto, type DTB 623, Copenhagen, Denmark) and are reported in Table 1 in comparison with literature data [19–21]. The density uncertainty was estimated to be $\pm 1.5 \times 10^{-5}$ cm^{-3}.

3. Correlation of the calorimetric data

The H_m^Es were obtained 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 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.

Each set of experimental values of H_m^E was fitted to a Redlich–Kister polynomial of the type:

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

an unweighted least-squares method, where x_1, x_2 are the molar fractions of glycols or PEGs (component 1) and component 2, whereas a_k are adjustable parameters. The a_k values are given in Table 2 together with the standard deviation $\sigma(H_m^E)$ defined as

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

where N and n are the number of experimental points and of parameters, respectively and $\phi_{\min}$ is the minimum value of

Table 2
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) + ethyl alcohol (component 2) at 308.15 K

Mixture	a_0	a_1	a_2	a_3	a_4	$\sigma(H_m^E)$ (J mol^{-1})
EG + EtOH	2165.3	−448.4	842.7	−152.1		2.8
DEG + EtOH	1080.2	−366.3	391.7	−146.5		1.8
TEG + EtOH	2503.3	−147.1	1316.8	−777.7		4.9
TETG + EtOH	3019.0	−109.8	877.8	−1612.2		4.2
PEG-200 + EtOH	2257.3	−90.6	984.1	−2274.5		5.2
PEG-300 + EtOH	2897.0	−918.6	−66.0	−1998.7	2415.5	7.4
PEG-400 + EtOH	3705.5	−1293.0	−2250.4	−2221.0	6603.2	7.5
PEG-600 + EtOH	4973.4	−2520.7	−5507.1	−2138.5	10930.9	8.3
Mix1 + EtOH	3985.1	−391.1	1591.3	−3030.9		7.0
Mix2 + EtOH	4085.4	−465.4	1651.4	−2834.8		8.1
Mix3 + EtOH	3901.3	−20.3	1604.9	−3659.9		6.3

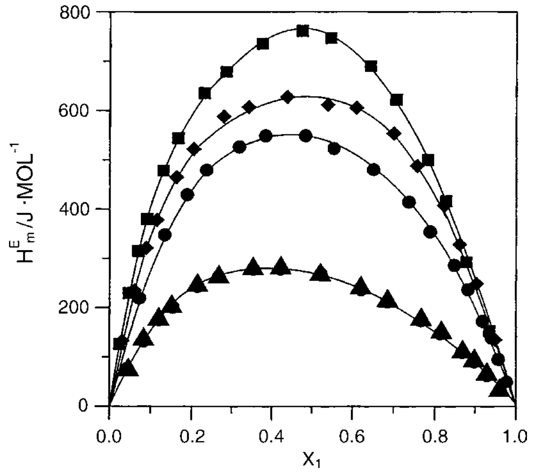

Fig. 1. Experimental excess molar enthalpies, H_m^E, for binary mixtures of glycols (1) + ethyl alcohol (2) at 308.15 K. (●), (▲), (♦), (■) refer to mixtures containing ethylene glycol, diethylene glycol, triethylene glycol, and tetraethylene glycol respectively. Solid curves, Redlich–Kister equation.

the objective function ϕ defined as

$$\phi = \sum_{k=1}^{N} \xi_k^2 \tag{5}$$

where $\xi_k = H_{m,calcd}^E - H_m^E$; H_m^E is the experimental value and H_m^E is evaluated by Eq. (3).

4. Results and conclusions

Experimental H_m^E's are represented in Figs. 1–3 together with the calculated values, $H_{m,calcd}^E$ (solid lines), evaluated from Eq. (3).

As can be seen from Figures, all H_m^E's are positive due to the high association of the ethyl alcohol, whose hydrogen bonds must be broken in the formation of the mixture. H_m^E decreases with the increase of molecular weight both for glycols and PEGs, a trend which is in a direction contrary to the one observed for the same glycols and PEGs with different solvents [22–24].

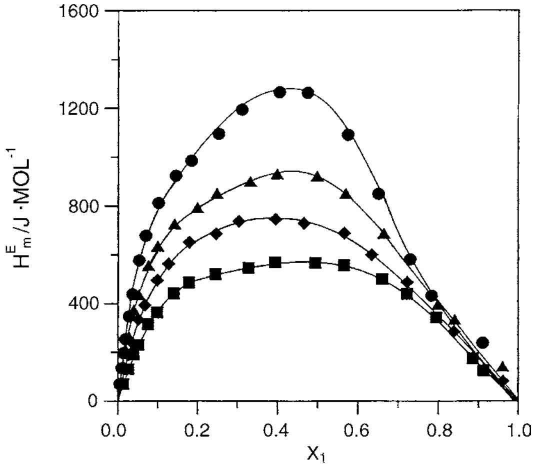

Fig. 2. Experimental excess molar enthalpies, H_m^E, for binary mixtures of PEGs (1) + ethyl alcohol (2) at 308.15 K. (■), (♦), (▲), (●) refer to mixtures containing PEG-200, PEG-300, PEG-400, and PEG-600, respectively. Solid curves, Redlich–Kister equation.

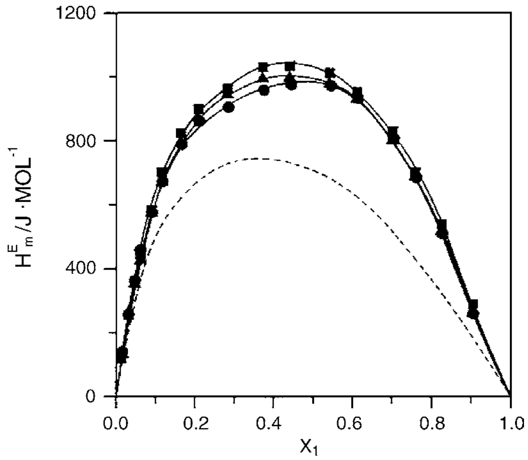

Fig. 3. Experimental excess molar enthalpies, H_m^E, for binary mixtures of mixtures of PEGs (1) + ethyl alcohol (2) at 308.15 K. (●), (■), (▲) refer to mixture mix1 (PEGs 300 + 400), mix2 (PEGs 200 + 400), and mix3 (PEGs 200 + 600), respectively. Dashed line refers to mixture containing PEG-300 as comparison. Solid curves, Redlich–Kister equation.

The influence of PEGs polydispersivity on H_m^E is stressed in Fig. 3 and, again, cannot compare with that resulting from mixtures with other solvents.

Clearly, the apparently anomalous behaviour of the mixtures containing ethyl alcohol is due just to the peculiar properties of that alcohol. The strong interactions among alcohol molecules leave unchanged some associations during mixing with the second component. Thus, interactions of E_{12} type between dissimilar molecules occur between PEGs and the residual alcohol associates rather than between PEGs and single alcohol molecules. This point of view is assumed elsewhere to explain for example the complex behaviour of ethanol in ternary mixtures [24] or to justify the mole interactions between short chain alcohol and polymers [25]. Following these lines, the results shown in Figs. 1–3, where longer chains of glycols or PEGs lead to smaller H_m^E values, may be due to a decrease of interaction between alcohol and solvent, as the chain is able to shield the O atoms more and more when its molecular size is increased. Different behaviour would be observed if single molecules of alcohol were available, owing to their interactions with the increasing number of O atoms in glycols and PEGs. Since E_{12} decreases as the size of solvent increase, the excess molar enthalpy, $H_m^E \approx E_{11} + E_{22} - 2E_{12}$, where E_{ij} is the interaction energy between molecules i and j, increases accordingly.

Moreover, Fig. 2 shows that the increase of H_m^E with increasing PEG molecular weight is larger in the alcohol rich region where, most probably, the size of alcohol associates is larger.

Only ethylene glycol is excluded from the behaviour just described, being its H_m^E larger than the one of diethylene glycol, and a possible interpretation of this result may be the larger value of E_{11} interaction energy.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at 10.1016/j.tca.2005.01.064.

References

[1] B.A. Andrews, J.A. Asenjo, Aqueous Two-Phase Partitioning, in: E. Harris, S. Angal (Eds.), Protein Purification Methods: A Practical Approach, IRL Press, Oxford, 1989.

[2] J.C. Merchuk, B.A. Andrews, J.A. Asenjo, J. Chromatogr. B: Biomed. Sci. Appl. 711 (1) (1998) 285–293.

[3] T.A. Graber, A.B. Andrews, J.A. Asenjo, J. Chromatogr. B: Biomed. Appl. 743 (2000) 57–64.

[4] R.D. Rogers, A.H. Bond, C.B. Bauer, J. Zhang, S. Griffin, J. Chromatogr. B: Biomed. Appl. 680 (1996) 221–229.

[5] S.K. Spear, S.T. Griffin, J.G. Huddleston, Ind. Eng. Chem. Res. 39 (9) (2000) 3173–3180.

[6] M.E. Taboada, T.A. Graber, B.A. Andrews, J.A. Asenjo, J. Chromatogr. B: Biomed. Appl. 743 (2000) 101–105.

[7] R.Y. Lochhead, J.V. Gruber, in: E.D. Goddard, J.V. Gruber (Eds.), Principles of Polymer Science and Technology in Cosmetics and Personal Care, Marcel Dekker, New York, 1999.

[8] R.L. Davidson, Handbook of Water Soluble Gums and Resins, McGraw-Hill Book Company, New York, 1980 (Chapter 18).

[9] L.H. Ninni, M.S. Camargo, A.J.A. Mereilles, Thermochim. Acta 328 (1999) 169–176.

[10] P. Sakellariou, M.H. Abraham, G.S. Whiting, Colloid Polym. Sci. 272 (1994) 872–875.

[11] B.A. Wolf, W. Schuch, Makromol. Chem. 182 (1981) 1801–1818.

[12] J.L. Koenig, A.C. Angood, J. Polym. Sci. A 2 (1970) 1787.

[13] R. Yang, X.R. Yang, D.F. Evans, W.A. Hendrickson, J. Baker, J. Phys. Chem. 94 (1990) 6123–6125.

[14] E. Sabadini, E.M. Assano, T.D.Z. Atvars, J. Appl. Polym. Sci. 63 (1997) 301–306.

[15] G.A. Jeffrey, W. Saenger (Eds.), Hydrogen Bonding in Biological Structures, Springer-Verlag, Berlin, 1991.

[16] P. Monk, I. Vadsö, Acta Chem. Scand. 22 (1968) 1842–1852.

[17] R. Francesconi, F. Comelli, J. Chem. Eng. Data 31 (1986) 250–253.

[18] J. Gmehling, J. Chem. Eng. Data 38 (1993) 143–146.

[19] E.A. Muller, P. Rasmussen, J. Chem. Eng. Data 36 (1991) 214–216.

[20] B.V.K. Naidu, K.C. Rao, M.C.S. Subha, J. Chem. Eng. Data 47 (2002) 379–382.

[21] G. Papanastasiou, A. Papoutsis, G. Kokkinidis, Bull. Soc. Chim. Fr. 4 (1987) 589–593.

[22] F. Comelli, S. Ottani, R. Francesconi, C. Castellari, J. Chem. Eng. Data 48 (2003) 995–998.

[23] C. Castellari, F. Comelli, R. Francesconi, Thermochim. Acta 413 (2004) 249–253.

[24] F. Comelli, S. Ottani, D. Vitalini, R. Francesconi, Thermochim. Acta 407 (2003) 85–92.

[25] E. Vercher, M.P. Pena, A. Martinez-Andreu, J. Chem. Eng. Data 39 (1994) 316–319.