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Excess molar enthalpies of binary mixtures containing poly(ethylene glycol) 200 + four cyclic ethers at (288.15, 298.15 and 313.15) K and at atmospheric pressure

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Abstract

Excess molar enthalpies, H_m^E, of binary mixtures containing poly(ethylene glycol) (PEG) 200 + 1,3-dioxolane, PEG 200 + 1,4-dioxane, PEG 200 + oxolane and PEG 200 + oxane were determined using a flow microcalorimeter at (288.15, 298.15 and 313.15) K and at atmospheric pressure. The H_m^E curves are always positive, with maxima varying from 393 J mol^{-1} (1,3-dioxolane) to 658 J mol^{-1} (oxolane), showing asymmetrical trends. The effect of the temperature is well marked on the calorimetric data that increase as the temperature is increased. The Redlich–Kister polynomial was used to estimate the binary fitting parameters. Root-mean-square deviations from the regression lines are reported.

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

1. Introduction

The thermodynamic and bulk properties of systems formed by mixing poly(ethylene glycol) (PEG) with organic solvents are of practical interest, because PEG is widely used in industrial processes, especially in the pharmaceutical, petroleum, cosmetic, textile and food industries [1,2]. Moreover, in recent years, the development of more environmental friendly processes, like the design of water soluble catalysts, drove further attention on the solution properties of PEG mixtures with organic solvents. Such properties have become important also in biotechnology, for extraction, separation and purification of biological substances [3–5].

As part of our experimental research program on the physicochemical properties of binary liquid mixtures containing PEG as a component [6,7], we report in this paper measurements of excess molar enthalpies, H_m^E, for binary mixtures containing PEG 200 + 1,3-dioxolane, PEG 200 + 1,4-dioxane, PEG 200+oxolane (tetrahydrofuran), and PEG 200+oxane (tetrahydropyran) at (288.15, 298.15 and 313.15) K. Data were collected at atmospheric pressure over the whole mole fraction range. In a previous paper [6] we have determined densities, viscosities and refractive indices of PEG 200 with the same cyclic ethers at 303.15 K. From the present measurements, values of H_m^E and the corresponding standard deviations, $\sigma(H_m^E)$, were calculated and fitted to the Redlich–Kister polynomial. The aim of this work is to extend the set of known excess properties for these systems and to interpret these properties in terms of

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molecular interactions between components. To our knowledge, there are no previous reports on these properties for the systems studied in the present paper.

2. Experimental

2.1. Chemicals

PEG 200, purchased from Fluka, was used without further purification. Molecular weight was obtained previously by gel permeation chromatography (GPC) and ESI mass spectrometric analysis [6]. 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 weight M_i, and weight fraction w_i. A polydispersity index was obtained as the ratio of M_w/M_n. The values obtained for PEG 200 are $M_n = 192$ and $M_w/M_n = 1.165$. 1,3-Dioxolane (Aldrich >99.8%), 1,4-dioxane (Fluka >99.8%), oxane (Aldrich >99%) and oxolane (Aldrich >99.9%) were also used without further purification. The stated purities from purchaser were checked and confirmed with the aid of a gas chromatograph (Hewlett-Packard, model 5890) using an HP (cross-linked 5% Me siloxane) capillary column. The purities of the pure components were also checked by comparing the measured densities, ρ, with those reported in literature [8–11] and results are shown in Table 1. Densities, ρ, 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 and capable of a precision greater than $\pm 1 \times 10^{-5}$ g cm^{-3}. The operating procedure of the apparatus was described previously [12].

Before measurements cyclic ethers were degassed by ultrasound (ultrasonic bath, Hellma, type 460, Milan, Italy). All chemicals were kept in dark bottles and dried over molecular sieves (Union Carbide, type 4A, 1/16 in. pellets).

2.2. Calorimetric measurements

H_m^E measurements were obtained by a flow microcalorimeter (LKB Producer, model 2107, Bromma, Sweden) operating on the heat-leakage principle [13] in flow conditions, equipped with two automatic burettes (ABU, Radiometer, Copenhagen, Denmark) to pump the pure liquids into the mixing cell of the calorimeter. The calibration of the apparatus and its operating procedure were described elsewhere [13,14]. The temperature of the calorimeter was kept constant to ±0.01 K, and mole fractions x_1 of PEG 200 were determined from flow rates, as stated by the automatic burettes. Flow rates were selected to cover the entire mole fraction range. Over the most of the mole fraction range the uncertainty in H_m^E and mole fraction were estimated to be less than 1% and 3×10^{-4}, respectively. Miscibility of the components was tested prior to measurements. Components were found to be completely miscible over the whole temperature and concentration range [6].

Before measurements, the calorimeter was checked using the test mixture cyclohexane+hexane, for which literature values are well known [15]. Agreement between calibration and literature data was better than 0.5% over the central range of mole fraction of cyclohexane.

Table 1
Densities, ρ, of pure chemicals and comparison with literature

Component	T (K)	ρ (g cm^{-3})	
		Experiment	Literature
PEG 200	288.15	1.12882	–
	298.15	1.12098	–
	313.15	1.10890	–
1,3-Dioxolane	288.15	1.07106	–
	298.15	1.05882	1.05865 [8]
1,4-Dioxane	288.15	1.03925	–
	298.15	1.02800	1.02797 [8]
	313.15	1.01118	1.0122 [9]
Oxolane	288.15	0.89263	–
	298.15	0.88190	0.88193 [10]
	313.15	0.86530	0.8653 [11]
Oxane	288.15	0.88920	–
	298.15	0.87931	0.8791 [8]
	313.15	0.86415	0.8638 [11]

3. Correlation of the calorimetric data

The experimental results of the excess molar enthalpies, H_m^E, for the four PEG 200 (1) + cyclic ethers

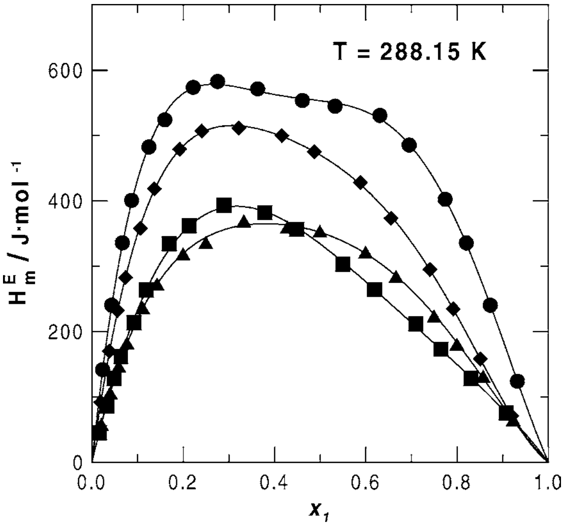

Fig. 1. Excess molar enthalpies, H^E_m, of binary mixtures containing PEG 200 + 1,3-dioxolane (■), PEG 200 + 1,4-dioxane (▲), PEG 200 + oxolane (◆) and PEG 200 + oxane (●) at 288.15 K. Full lines correspond to the Redlich–Kister polynomial.

(2) binary mixtures at the three test temperatures are listed in Table 2 and plotted in Figs. 1–3. Fig. 4 shows H^E_m $(x_1 = 0.5)$, the equimolar excess enthalpy plotted against the temperature values, T (K).

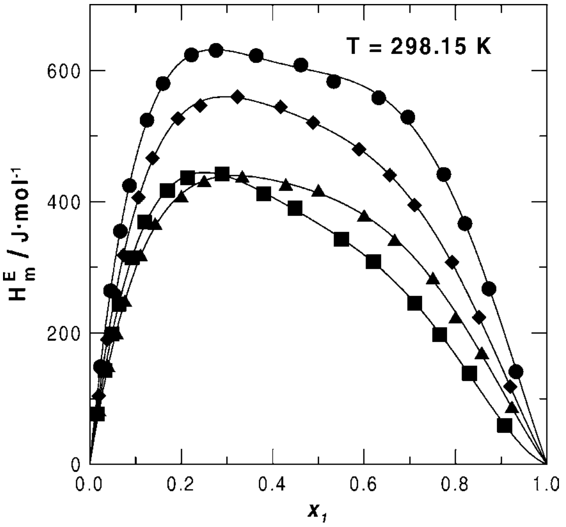

Fig. 2. Excess molar enthalpies, H^E_m, of binary mixtures containing PEG 200 + 1,3-dioxolane (■), PEG 200 + 1,4-dioxane (▲), PEG 200 + oxolane (◆) and PEG 200 + oxane (●) at 298.15 K. Full lines correspond to the Redlich–Kister polynomial.

Table 2
Excess molar enthalpies, H^E_m, of binary mixtures containing PEG 200 + 1,3-dioxolane, PEG 200 + 1,4-dioxane, PEG 200 + oxolane and PEG 200 + oxane in the range 288.15–313.15 K

x_1	H^E_m (J mol^{-1})	x_1	H^E_m (J mol^{-1})
PEG 200 + 1,3-dioxolane			
T = 288.15 K			
0.0167	45.4	0.3790	382.0
0.0328	86.0	0.4485	356.6
0.0484	128.1	0.5495	303.3
0.0635	162.0	0.6193	264.3
0.0923	213.5	0.7093	211.8
0.1194	263.7	0.7649	173.0
0.1690	334.5	0.8299	128.1
0.2132	362.0	0.9071	75.3
0.2891	393.0		
T = 298.15 K			
0.0167	77.0	0.3800	412.3
0.0329	143.1	0.4496	390.1
0.0486	198.9	0.5507	342.3
0.0637	244.0	0.6203	308.4
0.0927	314.9	0.7103	245.8
0.1198	368.9	0.7657	197.6
0.1696	417.4	0.8306	138.3
0.2140	436.5	0.9075	59.4
0.2901	442.5		
T = 313.15 K			
0.0168	89.0	0.3817	523.8
0.0331	164.2	0.4513	488.1
0.0489	228.9	0.5524	422.3
0.0641	283.3	0.6220	374.7
0.0932	368.3	0.7117	285.8
0.1206	423.2	0.7669	232.1
0.1706	499.7	0.8316	157.3
0.2151	532.5	0.9080	71.0
0.2914	545.5		
PEG 200 + 1,4-dioxane			
T = 288.15 K			
0.0203	58.3	0.4279	360.1
0.0399	106.4	0.4992	353.8
0.0587	147.4	0.5993	321.6
0.0767	182.7	0.6660	284.6
0.1108	236.6	0.7494	223.8
0.1425	273.2	0.7995	180.9
0.1995	319.2	0.8568	131.8
0.2493	336.4	0.9229	65.1
0.3326	369.5		
T = 298.15 K			
0.0204	82.6	0.4289	426.3
0.0400	150.4	0.5002	417.5
0.0589	200.1	0.6002	379.2
0.0770	249.6	0.6668	342.1
0.1112	318.9	0.7502	284.4
0.1429	366.7	0.8001	224.6

Table 2 (*Continued*)

x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})
0.2001	408.5	0.8573	170.4
0.2501	431.9	0.9231	87.6
0.3336	438.7		
$T = 313.15$ K			
0.0205	90.2	0.4303	535.5
0.0402	170.1	0.5016	512.0
0.0592	235.3	0.6016	463.1
0.0774	295.2	0.6681	423.1
0.1118	369.0	0.7512	360.4
0.1436	438.3	0.8010	312.6
0.2010	509.2	0.8580	245.2
0.2511	543.0	0.9235	147.4
0.3348	557.7		
PEG 200 + oxolane			
$T = 288.15$ K			
0.0194	92.0	0.4161	499.9
0.0381	169.9	0.4871	475.2
0.0560	232.3	0.5876	428.2
0.0733	282.8	0.6551	373.5
0.1061	358.0	0.7403	295.0
0.1367	418.7	0.7916	234.6
0.1919	479.3	0.8507	158.0
0.2404	506.9	0.9194	71.1
0.3220	511.6		
$T = 298.15$ K			
0.0195	104.2	0.4174	544.6
0.0383	190.2	0.4884	520.7
0.0563	260.9	0.5888	480.0
0.0737	318.3	0.6563	440.5
0.1066	406.4	0.7103	394.8
0.1373	466.6	0.7925	307.6
0.1927	526.8	0.8514	224.0
0.2414	546.4	0.9197	118.3
0.3232	560.0		
$T = 313.15$ K			
0.0197	104.2	0.4194	653.0
0.0386	192.0	0.4905	625.3
0.0567	265.2	0.5908	560.1
0.0742	327.2	0.6581	499.9
0.1074	423.4	0.7428	394.9
0.1382	492.8	0.7938	325.2
0.1940	582.2	0.8524	231.1
0.2428	624.6	0.9203	117.2
0.3249	658.4		
PEG 200 + oxane			
$T = 288.15$ K			
0.0232	141.7	0.4608	553.7
0.0430	240.6	0.5325	545.1
0.0665	335.9	0.6308	530.9
0.0867	400.8	0.6949	485.5
0.1246	482.7	0.7736	402.4
0.1595	524.1	0.8200	335.6
0.2216	573.8	0.8725	240.4
0.2751	582.9	0.9318	124.0
0.3629	571.6		
$T = 298.15$ K			
0.0232	148.7	0.4615	608.5
0.0455	264.7	0.5335	583.4
0.0667	354.9	0.6317	558.4
0.0870	424.5	0.6958	529.0
0.1250	524.3	0.7743	441.7
0.1601	580.4	0.8206	366.5
0.2223	623.9	0.8728	267.7
0.2760	630.8	0.9321	141.2
0.3639	622.7		
$T = 313.15$ K			
0.0234	160.0	0.4635	757.7
0.0458	289.1	0.5352	726.7
0.0671	395.3	0.6333	666.9
0.0875	479.0	0.6972	603.7
0.1258	613.0	0.7755	522.9
0.1610	678.2	0.8216	436.9
0.2235	760.0	0.8736	330.0
0.2773	785.8	0.9325	189.0
0.3653	787.1		

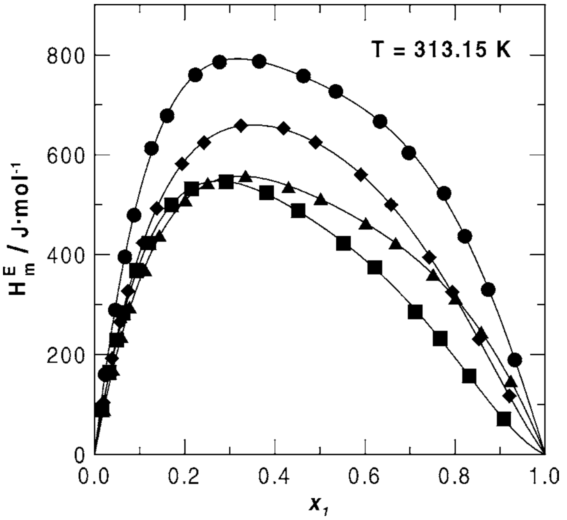

Fig. 3. Excess molar enthalpies, H_m^E, of binary mixtures containing PEG 200 + 1,3-dioxolane (■), PEG 200 + 1,4-dioxane (▲), PEG 200 + oxolane (◆) and PEG 200 + oxane (●) at 313.15 K. Full lines correspond to the Redlich–Kister polynomial.

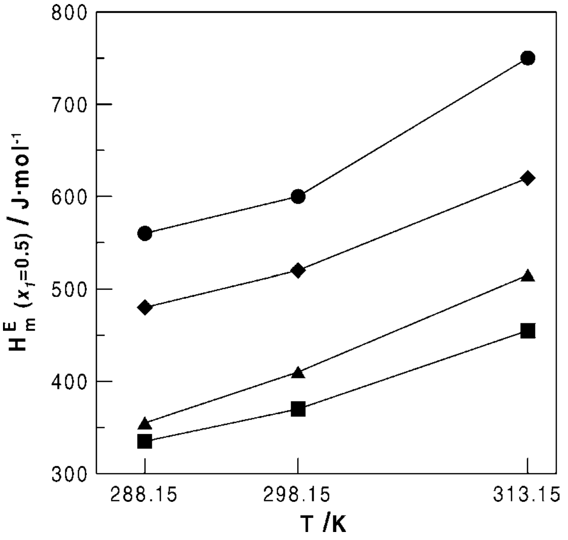

Fig. 4. Values of equimolar H_m^E $(x_1 = 0.5)$ as a function of test temperature, T (K), of PEG 200 + 1,3-dioxolane (■), PEG 200 + 1,4-dioxane (▲), PEG 200 + oxolane (◆) and PEG 200 + oxane (●).

To each of the 12 sets of experimental values, a Redlich–Kister polynomial of the type

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

has been fitted by a method of unweighted least-squares, where x_1 and x_2 are the molar fractions of PEG 200 and cyclic ethers, and a_k are the adjustable parameters. Values of a_k are reported in Table 3, together with the standard deviation $\sigma(H_m^E)$ defined as

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

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

$$\phi = \sum_{k=1}^{N} \xi_k^2 \qquad (3)$$

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

Data in Figs. 1–3 show that values of H_m^E are positive for all mixtures and temperatures and increase as the temperature is increased, with maxima corresponding to values of x_1 between 0.29 and 0.35, viz. in the ether-rich region. Moreover, H_m^E values of the diethers (1,3-dioxolane and 1,4-dioxane) are constantly lower than the corresponding values of monoethers (oxolane and oxane), except for a short region $(x_1 > 0.75)$ at the highest temperature. At equimolar composition (Fig. 4), diethers display quite similar values of H_m^E, a trend that is even more evident at the maximum values of H_m^E $(x_1 = 0.3)$.

4. Conclusions

Plots reported in Figs. 1–3 can be qualitatively analyzed by assuming that, at a first approximation,

Table 3
Least-squares parameters, a_k (J mol^{-1}), Eq. (1), and standard deviations, $\sigma(H_m^E)$, Eq. (2), of PEG 200 + cyclic ethers

Mixture	T (K)	a_0	a_1	a_2	a_3	$\sigma(H_m^E)$ (J mol^{-1})
PEG 200 + 1,3-dioxolane	288.15	1335.6	−1076.9	652.4	54.4	4.0
	298.15	1465.2	−852.7	1156.7	−1522.7	2.3
	313.15	1834.8	−1234.0	1140.1	−1370.5	2.3
PEG 200 + 1,4-dioxane	288.15	1407.4	−444.4	452.3	−749.8	3.4
	298.15	1652.5	−511.7	996.1	−1181.4	3.5
	313.15	2047.2	−847.7	1442.7	−452.2	2.6
PEG 200 + oxolane	288.15	1881.0	−829.1	917.9	−1469.6	2.3
	298.15	2086.0	−663.7	1450.9	−1577.9	2.3
	313.15	2481.1	−1008.2	944.5	−1171.4	1.5
PEG 200 + oxane	288.15	2213.3	−177.9	1927.2	−2381.1	4.1
	298.15	2391.9	−307.7	2153.3	−2236.0	4.3
	313.15	2967.0	−866.9	2287.0	−1399.3	4.7

$H_m^E \propto E_{11} + E_{22} - 2E_{12}$, where E_{ij} is the interaction energy between molecules of type i and j. Values of H_m^E are positive for all mixture and temperatures, so that $E_{11} + E_{22} > 2E_{12}$. Moreover, estimates of E_{22} from heats of vaporization [16] shows that for both diethers this term is equal to 35.6 J mol^{-1}, whereas for oxolane it is 32.0 J mol^{-1} and for oxane 34.9 J mol^{-1}. Data in these figures support the conclusion that E_{12} is larger for diethers as compared to mixtures of PEG with monoethers. Moreover, the greatest values of H_m^E for mixtures with oxane (see also data in Fig. 4) can be attributed to a smaller value of the interaction energy, E_{12}, since E_{22} is close to the values reported for the diethers.

These trends can be interpreted by the formation of intermolecular H-bonds between PEG and cyclic ethers. Strong H-bonds correspond to interactions between the terminal O–H groups of PEG and the O-atoms of the cyclic ethers, whereas H-bonds between the methylene group in the PEG chains and the ether O-atoms are weaker [17].

Actually, investigations on the solid-state structure of ethylene glycol show the presence of a three-dimensional network of H-bonds in the crystal [18]. Moreover, crystallographic data on α-, ω-alkanediols confirm that end groups are chained together via O–H···O bonds [19]. As regards PEG crystals, the polymeric chains are arranged in a 7_2 helix conformation [20]. In the molten state, PEG chains assume primarily a random coil form, this latter form is present also in chloroform and methylene chloride solutions [20]. In contrast, partial retention of the helix conformation has been reported for aqueous solutions of PEG [20], where H-bonds between –(CH_2–CH_2–O)– monomeric units and water have been detected [21]. These data suggest that, in the liquid state, PEG can develop a relatively extended network of intermolecular H-bonds. Hydroxyl groups in PEG molecules can act both as donors and acceptors. In contrast, ether group in both PEG and cyclic ethers can act only as acceptors. Actually, extended Hückel calculations performed by us on isolated molecules of the cyclic ethers show that their O-atoms bear localized negative charges of about −0.87. Thus, addition of cyclic ethers to PEG is expected to perturb mainly the H-bond network of the terminal –OH in PEG molecules. This perturbation should be especially significant for monoethers, because they can prevent extension of the network to additional molecules. Thus, smaller values of E_{12} for monoether mixtures lead to larger H_m^E. Additional support for this explanation can be obtained from data on excess viscosities. Negative deviations of the viscosity should correspond to a decrease in the number and strength of H-bonds in the solution, as compared to the pure components. This result has been reported for the same mixtures studied in this work, showing that excess viscosities are less (viz. more negative) for mixtures of PEG with monoethers [6].

Figs. 1 and 2 display a plateau-like feature around the maximum, extending towards higher polymer concentration. This particular shape is more evident for mixtures with oxolane and oxane, and tends to disappear as temperature is increased. Such a feature may correspond to the superposition of distinct contributions from strong and weak H-bonds. For aqueous solutions of PEG the coexistence of different hydrates have been reported. The hydration number of PEG depends on water concentration, increasing as the water molar fraction is increased [21]. It was concluded that more binding sites along the polymer chain become accessible at higher solvent concentration. We suggest that mixtures of PEG with cyclic ethers may display an analogous behavior. Weak H-bonds between the methylene groups in the PEG chains and the ether O-atoms start to form as the ether content is increased, leading to lower values of E_{12} per mole of PEG. Thus, larger excess molar enthalpies are obtained in the ether-rich region. The same effect would be responsible for the increase in the thermal effect (larger values of H_m^E) as the temperature is increased (Figs. 1–4). In aqueous solutions, H-bond complexes of PEG with water are destroyed if the solution is taken up above the melting point of pure PEG [22], likely by the collapse of the helical conformations of PEG chains. This conclusion seems to be consistent with the behavior of the systems studied in the present work. In fact, the reduction in the strength and number of H-bonds as the temperature is increased would lead to higher values of H_m^E.

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