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Excess molar enthalpies of binary mixtures containing glycols or (polyethylene) glycols + propylene carbonate at 308.15 K

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Abstract

Excess molar enthalpies, H_m^E, were determined as a function of molar fraction at 308.15 K and at atmospheric pressure for the binary mixtures containing propylene carbonate with ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, poly(ethylene glycol)-200, poly(ethylene glycol)-300, poly(ethylene glycol)-400, and poly(ethylene glycol)-600. Values of H_m^E range from a maximum of about 1640 J mol^{-1} (propylene glycol) to a minimum of about -386 J mol^{-1} (PEG-600). All mixtures containing monodisperse glycols have positive values of H_m^E. Also PEG-200 presents a curve of H_m^E versus x_1 (the molar fraction of glycol, component 1) always positive, whereas PEG-600 presents negative values of the heat of mixing over the whole range of the molar fraction. Finally, PEG-300 and PEG-400 show an inversion of sign of H_m^E, at about $x_1 = 0.7$ and 0.3, respectively. The experimental data were correlated using the Redlich–Kister polynomial and the adjustable parameters were obtained by the least-squares method. A qualitative discussion have been made in terms of intermolecular H-bonds.

Keywords: Excess molar enthalpy; Propylene carbonate; Poly(ethylene glycol); Calorimeter; Hydrogen bond

1. Introduction

The physical properties of binary mixtures are studied for many reasons, the most important of which is to provide information about molecular interactions present in the liquid state. In our previous studies [1–4], excess molar volumes, excess molar enthalpies, deviations in viscosities and refractive indices of binary mixtures containing poly(ethylene glycols) were determined. The poly(ethylene glycols) ($H(OCH_2CH_2)_nOH$) have found a wide variety of applications in the automotive, pharmaceutical, petroleum, cosmetic, textile, and other industries. Moreover, in recent years, attention has been focused on the solubility of PEGs in both water and organic solvents. This property is important in the development of more environmental friendly processes, like in the design of water soluble catalysts, and in the extraction, separation, and purification of biological substances. As a continuation of our work, the present paper deals with the excess molar enthalpies, H_m^E, of propylene carbonate (PCA) + ethylene glycol (EG), or +propylene glycol (PPG), or +diethylene glycol (DEG), or +triethylene glycol (TEG), or +tetraethylene glycol (TETG), or +PEG-200, or +PEG-300, or +PEG-400, or +PEG-600 at 308.15 K and at atmospheric pressure. Experimental measurements of H_m^E for the binary mixtures presented in this paper have not been found in the literature.

2. Experimental

Chemicals were used without further purification, degassed by using ultrasound (ultrasonic bath, Hellma, type 460, Milan, Italy) and dried over molecular sieves (Union Carbide, type 4A, 0.16 cm pellets) to reduce the water content before use.

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). The density meter precision was estimated to be $\pm 1.5 \times 10^{-5}$ g cm^{-3}. Details of the equipment and its

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Table 1
Purity, source, and density, ρ, of pure components and comparisons with literature data

Component	T (K)	ρ (g cm^{-3})	
		Experimental	Literature
Ethylene glycol (+99%) (Aldrich)	298.15	1.10980	1.10982[6]
	308.15	1.10293	1.10294[7]
Diethylene glycol (99%) (Aldrich)	298.15	1.11233	1.1122[8]
	308.15	1.10565	1.10557[7]
Triethylene glycol (99%) (Aldrich)	298.15	1.11980	1.11976[8]
	308.15	1.11210	1.11209[7]
Tetraethylene glycol (99%) (Aldrich)	298.15	1.12010	1.12005[8]
	308.15	1.11228	1.11228[9]
Propylene glycol (99.5%) (Riedel-de Haën)	308.15	1.02615	1.02617[7]
PEG-200 ($M_n = 192$; $M_w/M_n = 1.16$) (Fluka)	308.15	1.11284	1.11243[7]
PEG-300 ($M_n = 274$; $M_w/M_n = 1.11$) (Fluka)	308.15	1.11358	1.11328[7]
PEG-400 ($M_n = 365$; $M_w/M_n = 1.10$) (Fluka)	308.15	1.11489	1.11372[9]
PEG-600 ($M_n = 554$; $M_w/M_n = 1.06$) (Fluka)	308.15	1.11396	
Propylene carbonate (Fluka)	298.15	1.19952	1.1995[10]
	308.15	1.19024	

operating procedure have been described previously [5]. Purity, source, and density, ρ, of pure substances are shown in Table 1 and compared with literature data [6–10]. Both the number average, M_n $(=\sum N_i M_i/\sum N_i)$, and the weight average molecular weights, M_w $(= \sum N_i M_i^2/\sum N_i M_i = \sum w_i M_i)$, of PEGs were obtained by the gel permeation chromatography [1]. N_i is the number of moles of species i, having molecular weight M_i, and weight fraction w_i. Moreover, a polydispersity index was calculated as the ratio of M_w/M_n (Table 1). The excess molar enthalpies, H_m^E, were measured by using a flow microcalorimeter (LKB Producer AB, model 2107, Bromma, Sweden) equipped with a thermostatic water bath, a digital unit for data acquisition, and two automatic burets (ABU, Radiometer, Copenhagen) to pump pure liquids into the mixing cell of the calorimeter. The temperature of the heat sink containing both the mixing and reference cells was controlled by a water bath. Accuracy in temperature control is ±0.01 K. Details of the apparatus were reported in previous papers [11,12].

The H_m^E were obtained from the following relationship

$$H_m^E = \frac{I^2 R(E/E_c)}{f} \tag{1}$$

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 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

$$f_i = \frac{\rho_i V_i}{M_i} \tag{2}$$

where ρ_i and M_i are the density and molar mass, respectively, and V_i the volumetric flow rate of component i.

The performance and reliability of the calorimeter were checked by the test mixtures hexane + cyclohexane, benzene + cyclohexane, and methanol + water. The experimental excess molar enthalpies, agreed within 1% with the literature data [13]. Values of H_m^E of all mixtures are reported in Table 2. Each set of experimental values of H_m^E was fitted to a Redlich–Kister polynomial of the type

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

by an unweighted least-squares method. In Eq. (3), x_1, x_2 are the molar fractions of glycols or PEGs (component 1) and component 2 and a_k are adjustable parameters. The a_k values are given in Table 3 together with the standard deviation $\sigma(H_m^E)$ defined as

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

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

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

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

Table 2
Excess molar enthalpies, H_m^E, for binary mixtures containing propylene carbonate with ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, PEG-200, PEG-300, PEG-400 and PEG-600 at 308.15 K

x_1	H_m^E (J mol^{-1})
Ethylene glycol (1) + propylene carbonate (2)	
0.0597	644.7
0.1127	1003.1
0.1600	1205.9
0.2025	1313.6
0.2759	1441.3
0.3369	1479.6
0.4325	1459.7
0.5039	1393.7
0.5993	1254.2
0.6957	1071.2
0.7530	954.8
0.8205	807.5
0.8591	702.9
0.9014	571.9
0.9242	474.3
0.9482	355.4
0.9734	204.3
Propylene glycol (1) + propylene carbonate (2)	
0.0459	583.2
0.0879	962.7
0.1263	1215.2
0.1616	1377.2
0.2208	1553.2
0.2782	1635.0
0.3664	1665.9
0.4353	1639.7
0.5362	1552.6
0.6344	1428.8
0.6982	1338.8
0.7763	1190.3
0.8223	1065.9
0.8741	872.8
0.9025	750.1
0.9328	574.6
0.9652	333.6
Diethylene glycol (1) + propylene carbonate (2)	
0.0350	298.7
0.0693	516.7
0.1005	662.2
0.1296	765.9
0.1826	883.5
0.2295	930.6
0.3088	953.2
0.3733	927.2
0.4716	878.2
0.5727	804.0
0.6412	745.0
0.7283	648.8
0.7814	563.3
0.8428	446.7
0.8773	365.1
0.9147	266.1
0.9555	151.0
Triethylene glycol (1) + propylene carbonate (2)	
0.0258	215.6
0.0503	376.3
0.0736	496.1
0.0957	584.8
0.1370	696.0
0.1747	756.4
0.2410	793.3
0.2974	784.0
0.3884	764.1
0.4879	728.0
0.5595	681.0
0.6558	606.1
0.7176	533.0
0.7922	415.5
0.8356	332.9
0.8840	236.9
0.9385	121.6
Tetraethylene glycol (1) + propylene carbonate (2)	
0.0201	120.7
0.0393	213.7
0.0578	285.3
0.0757	342.1
0.1094	425.4
0.1407	463.1
0.1972	502.8
0.2466	521.4
0.3293	511.0
0.4242	499.3
0.4956	482.8
0.5957	417.6
0.6627	357.6
0.7467	261.6
0.7971	212.1
0.8550	144.2
0.9218	76.9
PEG-200 (1) + propylene carbonate (2)	
0.0203	158.4
0.0398	274.7
0.0585	361.6
0.0765	423.2
0.1105	490.3
0.1422	520.2
0.1991	534.8
0.2489	520.3
0.3320	490.5
0.4272	474.4
0.4986	464.2
0.5986	419.6
0.6654	367.0
0.7490	288.4
0.7991	227.2
0.8565	161.7
0.9227	93.2
PEG-300 (1) + propylene carbonate (2)	
0.0143	65.0
0.0282	116.6
0.0418	155.6
0.0549	183.0
0.0802	220.4
0.1041	241.4
0.1484	243.3
0.1885	232.0
0.2584	199.6
0.3434	167.9
0.4108	148.2
0.5112	111.9
0.5824	74.9
0.6766	12.1
0.7361	−21.7

Table 2 (*Continued*)

x_1	H^E_m (J mol^{-1})
0.8071	−36.0
0.8932	−20.6
0.9177	−9.6
PEG-400 (1) + propylene carbonate (2)	
0.0079	18.0
0.0157	34.0
0.0317	59.3
0.0418	70.4
0.0614	81.5
0.0802	85.0
0.1158	79.1
0.1485	63.5
0.2074	35.6
0.2820	−2.3
0.3437	−17.5
0.4399	−39.4
0.5115	−58.0
0.6111	−94.5
0.6768	−121.8
0.7586	−133.7
0.8627	−91.0
0.8934	−70.0
PEG-600 (1) + propylene carbonate (2)	
0.0139	−25.5
0.0208	−36.2
0.0275	−47.7
0.0407	−62.6
0.0536	−86.9
0.0782	−120.8
0.1016	−151.0
0.1471	−198.6
0.2055	−249.8
0.2565	−290.0
0.3410	−346.6
0.4082	−382.3
0.5086	−417.9
0.5798	−416.1
0.6743	−385.7
0.8054	−267.1
0.8466	−220.0
0.9501	−68.0

3. Discussion

Experimental H^E_m data are presented in Figs. 1 and 2 together with the calculated values $H^E_{m,calcd}$ (solid lines).

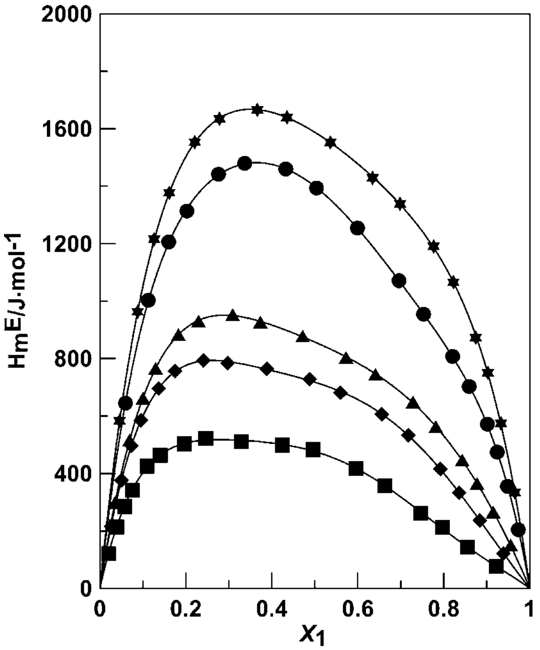

Fig. 1. Excess molar enthalpies, H^E_m, for binary mixtures of EG (1)+PPCA (2) (●) and PPG (1) + PPCA (2) (★), DEG (1) + PPCA (2) (▲), TEG (1) + PPCA (2) (◆) and TETG (1) + PPCA (2) (■) at 308.15 K. Solid curves represent Redlich–Kister equation.

The excess molar enthalpies of the solutions of PCA with monodisperse glycols are positive over the whole range of composition, according to the sequence PPG > EG ≫ DEG > TEG > TETG. The heat of mixing decreases with the increase of molecular size with the exception of PPG (Fig. 1). A decrease of H^E_m with the increase of molecular length is observed also for the solutions of PCA + PEGs (Fig. 2). The values at equimolar composition ($x_1 = 0.5$) are positive for PEG-200 and PEG-300 and negative for PEG-400 and PEG-600. In addition, the curve of PEG-200 is always positive, whereas PEG-600 presents negative values of the heat of mixing over the whole range of the molar fraction. The curves of PCA + PEG-200 and PCA + TETG practically overlap, since the molecular weights of the glycols are 200 and 194, respectively, and PEG-200 samples have a small value of polydispersity (Table 1).

Table 3

Least-squares parameters, a_k, Eq. (3), and standard deviations, $\sigma(H^E_m)$, Eq. (4), of glycols and (polyethylene)glycols containing propylene carbonate at 308.15 K

Mixture	a_0	a_1	a_2	a_3	a_4	$\sigma(H^E_m)$ (J mol^{-1})
Propylene carbonate + ethylene glycol	5597.7	−2321.3	1976.0	−241.1	3632.5	3.4
Propylene carbonate + diethylene glycol	3430.0	−1312.2	2807.2	−1782.5	395.1	2.3
Propylene carbonate + triethylene glycol	2870.2	−935.7	1933.8	−2836.0	849.3	2.8
Propylene carbonate + tetraethylene glycol	1905.6	−876.2	248.3	−1924.4	1748.0	3.5
Propylene carbonate + propylene glycol	6350.4	−1862.5	4413.8	−242.7	2180.2	3.5
Propylene carbonate + PEG-200	1850.6	−466.2	412.6	−3158.7	2884.6	3.0
Propylene carbonate + PEG-300	471.5	−868.8	−756.5	−1408.6	3028.5	1.2
Propylene carbonate + PEG-400	−214.7	−610.0	−1065.8	−654.4	2482.9	1.7
Propylene carbonate + PEG-600	−1655.9	−392.2	75.5	658.1		2.1

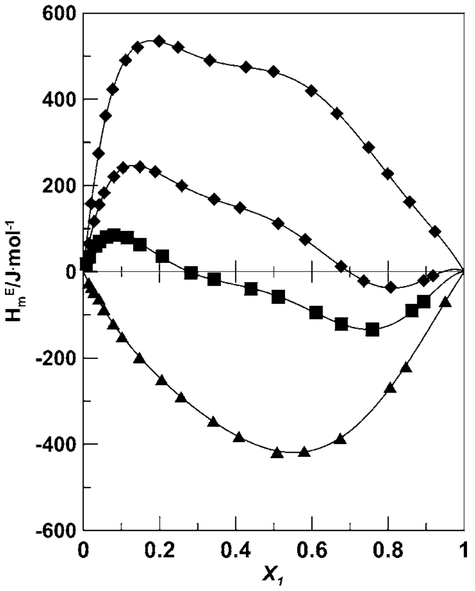

Fig. 2. Excess molar enthalpies, H_m^E, for binary mixtures of PEG-200 (1) + PPCA (2) (●), PEG-300 (1) + PPCA (2) (◆), PEG-400 (1) + PPCA (2) (■), PEG-600 (1) + PPCA (2) (▲), at 308.15 K. Solid curves represent Redlich–Kister equation.

An analysis of the experimental data can give some insights into the interactions between the components. If the H_m^E of a binary system at $x_1 = 0.5$ is approximated to the following equation:

$$H_m^E \propto +E_{22} - 2E_{12} \tag{6}$$

where E_{ij} is the interaction energy between molecules i and j. The term E_{11} takes into account mainly the cooperative hydrogen bonding between the terminal O–H groups of the glycol. However, as the number of ethereal groups in the chain increases, the interaction between the O–H groups must compete more and more with the interaction between the hydroxyl and the ethereal O atom. Since the latter type of interaction is weaker than the former, an increase of the chain length of the (oxyethylene)glycols leads to decreasing of the term E_{11} and a consequent lowering of the heat of mixing. However, propylene carbonate (component 2) has a large vaporization enthalpy (65 kJ mol^{-1}) and a large dipole moment (4.94 D) in agreement with the net charges calculated by us for the non-hydrogen atoms of PCA (Fig. 3). Moreover, X-ray diffraction data [14–16] give evidence of interactions of the type C–H · · · O, in which PCA is involved through the oxygen atom of the C=O group. As a consequence, it is reasonable to admit that the term E_{22} gives a significant contribution to the H_m^E of the mixtures studied. Actually, literature quotes studies on the self-association of the PCA [17,18].

As to the term E_{12} of Eq. (6), the intermolecular pattern can be mainly referred to the H-bonds formed between the terminal O–H groups of the glycol and the C=O group of the propylene carbonate. Except for the PPG–PCA mixtures, the contribute of the term E_{12} to the heat of mixing can be roughly considered constant for the binary systems studied. However, the data of Fig. 1 show that H_m^E of PPG–PCA mixture is larger than that of EG–PCA. This can be explained admitting that in PPG, the term $-2E_{12}$ gives a minor contribution to the heat of mixing, due to the steric hindrance of the methyl group that screens the adjacent oxygen atom.

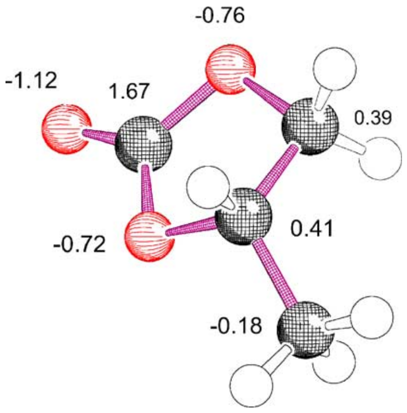

Fig. 3. Molecular conformation of PCA showing the net charges (*e*) resulting from the extended Hückel approximation (crystallographic coordinates from [19]).

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