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Effect of excess enthalpies on binary mixtures containing propylene glycols and poly(propylene glycols) + dimethyl carbonate at 308.15 K

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Abstract

Excess enthalpies have been determined at atmospheric pressure and at 308.15 K over the entire range of composition for binary mixtures containing propylene glycol (PG), dipropylene glycol (DPG), tripropylene glycol (TPG), poly(propylene glycol)-400, -725, -1200, -2000 + dimethyl carbonate (DMC). From the experimetal data, excess enthalpies, H^E, and standard deviations in enthalpy, $\sigma(H^E)$ have been calculated. The experimental data were fitted to a Redlich–Kister polynomial to obtain the binary adjustable parameters, a_k. The H^E values are positive over the entire range of composition, decreasing with the increase of the molecular weight of glycols. The mixtures containing polydisperse glycols behave as regular solutions. Conclusions were qualitatively discussed in terms of molecular interactions.

Keywords: Excess enthalpy; Polymers; Calorimeter; Correlation data

1. Introduction

This work continues our study on the thermodynamic properties of binary mixtures containing glycols and polyglycols [1–3]. These compounds have found a wide variety of applications in the automotive, petroleum, cosmetic, texile, and other industries. Particularly, propylene glycol (PG) is widely used in pharmaceutical manufacturing as a solvent and vehicle especially for drugs unstable or insoluble in water. It may also be employed as a stabiliser in vitamin preparation and in veterinary medicine as a glucose precursor [4,5].

We present, in this paper, measurements of excess enthalpies, H^E, at 308.15 K of the binary systems containing glycols H-[OP]$_j$-OH, where OP is the monomeric unit $OCH_2CH(CH_3)$, and dimethyl carbonate (DMC). We chose monodisperse compounds: propylene glycol ($j = 1$), dipropylene glycol (DPG) ($j = 2$), tripropylene glycol (TPG) ($j = 3$) as well polydisperse ones of different nominal molecular weight: (PPG)-400, -725, -1200, -2000. The aim of this paper is to check the influence of both the –OH end-groups and ether oxygen atoms (when $j > 1$) of the glycols on the molecular interactions present in the mixtures of DMC, a aprotic solvent of great technological importance used in the electrolyte of lithium batteries. No measurements on enthalpy for these systems are available in the literature. The experimental results reveal the effects of composition and molecular structure on the heat of mixing.

2. Experimental

2.1. Chemicals

1,2-Propylene glycol is a Riedel-deHaën product, dipropylene glycol, tripropylene glycol, poly(propylene glycol)-725, dimethyl carbonate are from Aldrich, while poly(propylene glycols)-400, -1200, -2000 are Fluka products. Dimethyl carbonate and propylene glycols show purities ≥99 mol% and were subjected to no further purification other than being dried with Union Carbide, type 4A, 1/16 in. pellets molecular sieves before measurements. Also PPGs were used without further purification.

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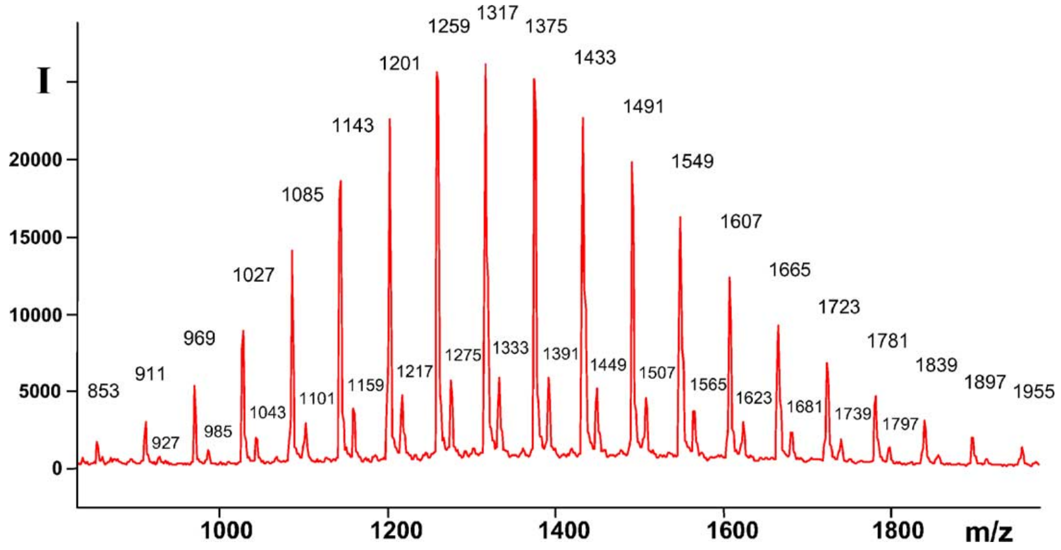

Fig. 1. Positive MALDI-TOF mass spectrum of a PPG-1200 sample.

2.2. Molecular weights of polymeric samples

Molecular weights of polymeric samples (PPG) were obtained by MALDI-TOF mass spectrometric analysis (Voyager DE-STR from PerSeptive Biosystem), using *trans*-3-indoleacrylic acid as a matrix. The number average, M_n ($\Sigma N_i M_i/\Sigma N_i$), 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 M_w/M_n. As an example, the MALDI mass spectrum of PPG-1200 is reported in Fig. 1. The spectrum is constituted essentially of two series of peaks at m/z 853 + n58 and m/z 927 + n58, corresponding to molecules of PPG di-hydroxy terminated H-[OP]$_j$-OH cationized with Na^+ and K^+, respectively, and only traces of PPG molecules cationized with H^+ or Li^+ are present. No peaks due to impurities are detected, so that the sample can be considered substantially pure.

Also in a previous work on PEGs [1], the determination of the molecular weight of the polymers has been attempted by means of the MALDI-TOF mass spectrometry. However, only qualitative information about the purity of the samples were obtained as a consequence of the too low molecular weight of some samples (200–300 Da). In these cases, under high vacuum conditions, the composition of the mixtures was altered after the introduction into the ion source of the mass spectrometer. On the contrary, PPGs samples analyzed in this study have higher MW than the formers, so that their composition is not changed also after quite a long time under high vacuum. For this reason, their MALDI mass spectra not only give information about their composition and purity, but permit also of calculating their molecular weights and polydispersities.

The values obtained for PPGs-400, -725, -1200, -2000 are $M_n = 502$ ($j_{av} = 8.3$), 856 ($j_{av} = 14.4$), 1335 ($j_{av} = 22.7$) and 2004 ($j_{av} = 34.2$) and $M_w/M_n = 1.020$, 1.033, 1.029 and 1.029, respectively, where j_{av} is the average number of OP units. The higher M_W values obtained by MALDI with respect to those given from the suppliers (GPC data) are in agreement with the different techniques utilised.

2.3. Densities and calorimetric measurements

The densities, ρ, of pure chemicals were measured using a digital density meter (Anton Paar, model 60, Graz, Austria) equipped with a measuring cell (type 602) operated in the static mode with an accuracy of $\pm 1.10^{-5}$ g cm^{-3}.

The density data are shown in Table 1, but only two values can be compared with those of literature [6,7]. Before measurements, all chemicals were degassed by ultrasound (ultrasonic bath, Hellma, type 460, Milan, Italy) and kept in dark bottles.

The enthalpy changes of mixing, H^E, were obtained by a flow type isothermal microcalorimeter (model 2107, LKB Producer, Bromma, Sweden). The apparatus consists of a

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

Component	ρ (g cm^{-3})	
	Experimental	Literature
Propylene glycol	1.02615	1.02617 [6]
Dipropylene glycol	1.01046	–
Tripropylene glycol	1.00487	–
Poly(propylene glycol)-400	0.99568	–
Poly(propylene glycol)-725	0.99353	
Poly(propylene glycol)-1200	0.993031	–
Poly(propylene glycol)-2000	0.99212	–
Dimethyl carbonate	1.049826 1.06307[a]	−1.06306 [7][a]

[a] At 298.15 K.

flow-mixing cell, a reference cell, a thermostatic water bath, a data acquisition unit, and two automatic burets (ABU, Radiometer, Copenhagen, Denmark) necessary to pump the pure liquids into the mixing cell of the calorimeter. The temperature of the bath was controlled within ±0.01 K. The calibration of the apparatus and its operating procedure were described elsewhere [8,9]. 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 with literature data [10]. Miscibility of the components was tested prior to measurements and components were found to be completely miscible over the whole concentration range. Weight fractions, w_1, of both monodisperse propylene glycols and PPGs were computed from densities; volumetric flow rates of components, selected to cover the entire weight fraction range, were stated by the automatic burettes. The experimental uncertainties in H^E were estimated to be less than 0.5% over the most of the composition range.

Table 2
Excess enthalpies, H^E (J g^{-1}), vs. weight fraction w_1 of binary mixtures containing propylene glycols or poly(propylene glycols) (1) + dimethyl carbonate (2) at 308.15 K

w_1	H^E (J g^{-1})	w_1	H^E (J g^{-1})	w_1	H^E (J g^{-1})
PG (1) + DMC (2)					
0.0391	6.24	0.3280	20.40	0.7961	13.08
0.0752	10.53	0.3941	20.85	0.8542	10.07
0.1088	13.50	0.4940	20.61	0.8865	8.31
0.1399	15.43	0.5943	19.19	0.9214	5.89
0.1930	17.77	0.6613	17.85	0.9591	3.21
0.2455	19.47	0.7455	15.24		
DPG (1) + DMC (2)					
0.0385	3.07	0.3246	12.81	0.7936	7.72
0.0741	5.51	0.3905	13.05	0.8523	5.88
0.1073	7.29	0.4901	12.73	0.8849	4.67
0.1380	8.75	0.5906	11.82	0.9202	3.15
0.1937	10.62	0.6578	10.76	0.9585	1.63
0.2426	11.78	0.7425	9.05		
TPG (1) + DMC (2)					
0.0383	1.99	0.3234	9.95	0.7927	6.65
0.0738	3.63	0.3891	10.56	0.8515	5.26
0.1067	5.01	0.4887	10.36	0.8844	4.18
0.1374	6.13	0.5892	9.71	0.9198	3.14
0.1929	7.70	0.6566	8.98	0.9582	1.64
0.2416	8.71	0.7617	7.27		
PPG-400 (1) + DMC (2)					
0.0380	0.72	0.3217	4.21	0.7914	3.28
0.0732	1.34	0.3873	4.56	0.8506	2.52
0.1060	1.86	0.4868	4.87	0.8835	2.04
0.1375	2.30	0.5873	4.73	0.9192	1.47
0.1917	2.97	0.6548	4.51	0.9599	0.78
0.2402	3.44	0.7399	3.79		
PPG-725 (1) + DMC (2)					
0.0379	0.48	0.3212	2.56	0.7910	2.19
0.0731	0.86	0.3868	2.76	0.8503	1.78
0.1058	1.20	0.4862	2.94	0.8833	1.48
0.1362	1.48	0.5868	2.91	0.9191	1.06
0.1913	1.87	0.6543	2.77	0.9578	0.60
0.2398	2.15	0.7395	2.44		
PPG-1200 (1) + DMC (2)					
0.0379	0.31	0.3211	1.89	0.7910	1.53
0.0731	0.57	0.3866	2.06	0.8502	1.17
0.1057	0.80	0.4861	2.24	0.8833	0.97
0.1362	1.04	0.5867	2.11	0.9190	0.70
0.1912	1.31	0.6542	2.02	0.9578	0.37
0.2397	1.57	0.7394	1.76		
PPG-2000 (1) + DMC (2)					
0.0379	0.25	0.3209	1.63	0.7908	1.34
0.0730	0.48	0.3864	1.76	0.8501	1.04
0.1057	0.68	0.4859	1.91	0.8832	0.86
0.1361	0.84	0.5865	1.92	0.9190	0.63
0.1911	1.14	0.6540	1.74	0.9578	0.33
0.2395	1.32	0.7393	1.57		

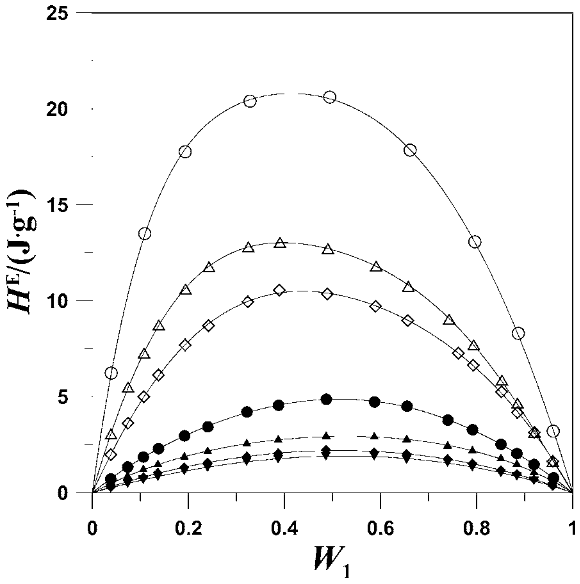

Fig. 2. Excess molar enthalpies, H^E, vs. weight fraction w_1, for binary mixtures of PG (1) + DMC (2) (○); DPG (1) + DMC (2) (△); TPG (1) + DMC (2) (◇); PPG-400 (1) + DMC (2) (●); PPG-725 (1) + DMC (2) (▲); PPG-1200 (1) + DMC (2) (◆); and PPG-2000 (1) + DMC (2) (▼) at 308.15 K. Solid curves, Redlich–Kister equation.

The experimental results of the excess enthalpies, H^E, for the seven mixtures containing propylene glycols (1) or PPGs (1) + DMC (2) are listed in Table 2 and plotted in Fig. 2 as a function of the weight fraction of (1).

3. Discussion

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

$$H^E_{\text{calcd}} = w_1 w_2 \sum_{k\geq 0} a_k (w_1 - w_2)^k \tag{1}$$

was fitted by a method of unweighted least-squares, where w_1 and w_2 are the weight fractions of the components and a_k are the adjustable parameters. Values of a_k are reported in

Table 3
Least-squares parameters, a_k, Eq. (1), and standard deviations, $\sigma(H^E)$, Eq. (2), of binary mixtures containing propylene glycols or poly(propylene glycols) (1) + dimethyl carbonate (2) at 308.15 K

Component (1)	PG	DPG	TPG	PPG-400	PPG-725	PPG-1200	PPG-2000
a_0	81.19577	50.98819	41.53827	19.44724	11.72220	8.80204	7.64318
a_1	−14.90831	−13.69277	−8.50284	1.10254	1.02639	0.47116	0.72146
a_2	46.00799	16.40488	8.98238	0.26096	2.75021	0.25162	0.15304
a_3	−35.03837	−9.98750	2.86854	−1.40555			
$\sigma(H^E)$	0.16	0.087	0.087	0.028	0.019	0.020	0.020

Table 3, together with the standard deviation $\sigma(H^E)$ defined as

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

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

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

where $\eta_k = H^E_{\text{calcd}} - H^E$.

The plots of Fig. 2 show positive values of H^E for all the mixtures studied. The endothermic effect decreases with increasing the number j of OP units in the glycol chains H-[OP]$_j$-OH. In order to determine whether the mixtures studied can be treated with the regular solution model, in Fig. 3 are plotted the values of $H^E/(w_1w_2)$, calculated for $w_1 \rightarrow 0$ and $w_1 \rightarrow 1$, as a function of the number of OP units, by means of the parameters of Eq. (1), quoted in Table 3. In this model $H^E \approx a_0w_1w_2$, where $a_0 \propto E_{11} + E_{22} - 2E_{12}$ is the first adjustable parameter (Table 3). Fig. 3 shows that $H^E/(w_1w_2)$ is independent of composition for each j, as postulated by regular solution model, only for polydisperse glycols. On the contrary, the mixtures containing monodisperse glycols ($j \leq 3$) do not behave as regular solutions.

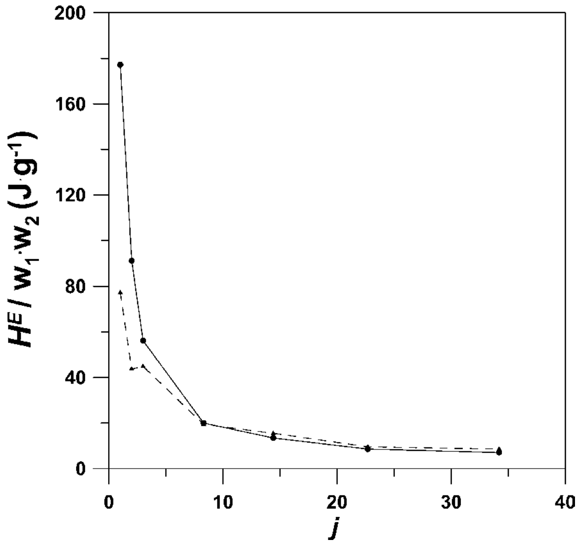

Fig. 3. Values of H^E/w_1w_2 at $w_1 \rightarrow 0$ ((●) and solid line) and H^E/w_1w_2 at $w_1 \rightarrow 1$ ((▲) and dotted line) as a function of the number j of the repeating units for the binary mixtures containing PG (1) + DMC (2), DPG (1) + DMC (2), TPG (1) + DMC (2), PPG-400 (1) + DMC (2), PPG-725 (1) + DMC (2), PPG-1200 (1) + DMC (2), and PPG-2000 (1) + DMC (2), respectively.

The importance of the hydrogen bonding in polymer mixtures [11] and solutions [12] has been shown. The terminal hydroxyls of the glycol chains H-[OP]$_j$-OH are hydrogen bonding donor and acceptor groups whereas the ether oxygen atom along the chain ($j > 1$) are acceptor. Ab initio calculations and molecular dynamics simulation [13,14] show that the molecule of DMC can assume in both gas and liquid state two conformations: *trans–trans* with C_{2v} point group symmetry (Fig. 4) and *trans–cis* with C_s point group. The *trans–cis* configuration energy was found 13.18 kJ mol^{-1} higher than the *trans–trans* [14]. The atomic charges (e) of the *trans–trans* conformer were the following: $O_1 = -0.68$, $C_1 = 1.09$, $O_{2\text{–}3} = -0.45$, $C_{2\text{–}3} = -1.16$, $H = 0.13$ [14]. It is clear that in the hydrogen bonding DMC acts as H-bond acceptor with the O_1 atom. Finally, the average molecular dipole moment in the liquid state was estimated to be 1.29 (D) [14].

Between the components (1) and (2) of the mixtures studied in the present work are thus possible hydrogen bonds of type $O\text{–}H_{(1)} \cdots OH_{(1)}$ $O\text{–}H_{(1)} \cdots O_{(1)}$, and $O\text{–}H_{(1)} \cdots O = C_{(2)}$. For these H-bonds, cristal structure data [15] show mean O–H · · · O bond lengths of 0.186, 0.185 and 0.219 nm, respectively. However, the former involves the terminal hydroxyl groups of the glycols and can originate finite or infinite chains that are stabilised by the σ-bond cooperativity [15].

On the basis of the discussion given above, we may consider that in the glycol molecule the increase of the number

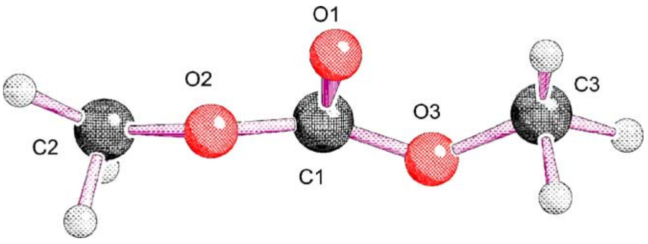

Fig. 4. Molecular diagram of *trans–trans* dimethyl carbonate.

of OP units corresponds to a gradual substitution of the $O–H_{(1)} \cdots OH_{(1)}$ bonds with the weaker $O–H_{(1)} \cdots O_{(1)}$ ones with the consequent decrease of the term E_{11}. In the mixtures, the molecule interaction between glycol and DMC involves, as said, the terminal hydroxy groups of the glycols and the C=O group of DMC. In this case, the effect of the increasing the number of the OP units in the glycol is low and E_{12} can be considered almost constant.

These considerations indicate that, for the mixtures containing polydisperse polymers, $H^E \propto E_{11}+E_{22}-2E_{12}$ will decrease with the increasing of j_{av}, in agreement with the plots of Fig. 2. However, the positive values of H^E show a sensible contribution of the term E_{22} to the heat of mixing. It is clear that the effect of intramolecular contacts of the type $CH \cdots O{=}C$ in DMC appears significant although vibrational frequencies of the molecule in both gas and liquid state result very close [13].

The plots of Fig. 2 referring to PG, DPG and TPG mixtures show a decrease of H^E with the increase of the OP units in the chain as in the case of the polydisperse glycols. The thermodynamic behaviour of the monodisperse glycols, which does not follow the regular solution model, further reflects the increase or the decrease in the population of the intra and intermolecular H-bonds above examined. However, the effects of these interactions can be interpreted in the terms E_{11}, E_{22} and E_{12} at a lower level of approximation than in the case of polydisperse glycols. Nevertheless, it should be remarked that PG mixture presents the highest value of H^E. This result implies that in absence of the ethereal group in the OP unit ($j = 1$), the less polar DMC does not attain the complete disruption of the σ-bond cooperativity extending to two o more molecules of PG.

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