

Excess enthalpies of binary mixtures containing poly(propylene glycols) + benzyl alcohol, or + *m*-cresol, or + anisole at 308.15 K and at atmospheric pressure

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Abstract

Excess enthalpies, H^E , of binary mixtures containing poly(propylene glycols) of different molecular masses + benzyl alcohol, or + *m*-cresol, or + anisole were determined using a flow microcalorimeter at 308.15 K and at atmospheric pressure. Data was correlated using the Redlich–Kister polynomial. Results were qualitatively discussed in terms of molecular interactions and of the regular solution model.
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Keywords: Excess enthalpy; Poly(propylene glycol); Calorimeter

1. Introduction

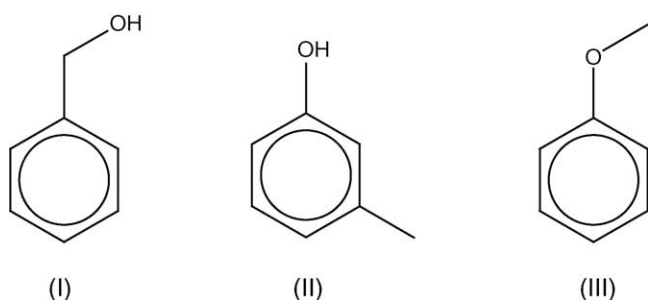
Poly(glycols) are widely employed in a variety of industrial processes [1] especially in binary and multicomponent mixtures with water and organic solvents. Poly(glycol) solutions in organic solvents display a wide range of thermodynamic properties depending on the composition and the type of solvent and also on the chemical structure and length of the polymer chain. For these systems two types of factors appear to dominate the relevant intermolecular and intramolecular interactions, determining solution properties. The first factor is the competition between hydrophilic and hydrophobic groups along the polymer chain. A second, and possibly more important, factor is the stability of the H-bond network that hydrophilic groups form among them and, eventually, with solvent molecules. As part of our research program on the excess properties of binary mixtures containing poly(glycols) [2–4], in the present work we report experimental excess enthalpies of mix-

ing, H^E , of binary mixtures containing poly(propylene glycols) of different molecular masses + benzyl alcohol, or + *m*-cresol or + anisole at 308.15 K and at atmospheric pressure.

Poly(propylene glycol) (PPG) is a linear chain polymer of oxypropylene units, $-\text{[CH}_2\text{CH(CH}_3\text{)O]}-$, terminated by hydroxyl groups at both ends. The etheric O-atom in the monomer unit and the $-\text{OH}$ group are strongly hydrophilic, while the aliphatic portions of the chains and the pendant methylene groups provide hydrophobic interactions. As compared to poly(ethylene glycol) (PEG), PPG is only partially soluble in water, due to the additional hydrophobic effect introduced by the methylene group. The methylene group is also responsible for the molecular glassformer nature of PPG, since it can prevent crystallization of the undercooled liquid [5–7]. Actually, the simultaneous presence of hydrophobic and hydrophilic groups may account for the solubility of this polymer in a large number of substances, as well as for its complex solution behavior. In fact, it has been reported that, upon mixing with polar solvents, like water, conformations of PPG chains change from random-coil (non-polar) to helical (polar) [8].

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Benzyl alcohol (**I**), *m*-cresol (**II**), and anisole (**III**), are three cyclic aromatic compounds, with the same molecular weight but different molecular structures. PPGs molecules can interact with these solvents by the etheric O-atoms and the hydroxyl end-groups. Interactions involve both weak (C··H–O) and strong (O··H–O) H-bonds. Upon mixing with the cyclic compounds, the H-bonds between polymer molecules can be perturbed and destroyed. It is the purpose of this paper to investigate the effect of different molecular structures of the solvent on the intermolecular and intramolecular interactions of several PPG grades by measuring changes in the excess enthalpies of mixing. Tentative correlations can be explored between such changes and modifications in the H-bond patterns governing molecular interactions in solutions. Data of this kind can be relevant and even critical for several practical applications and industrial processes.



Enthalpy data on mixtures containing PPGs are seldom found in the literature and no measurements have been previously reported for the mixtures studied in this work.

2. Experimental

2.1. Chemicals

Benzyl alcohol and *m*-cresol were Riedel-de-Haën products, while anisole was purchased from Aldrich. Purities of the compounds were 99.8, 99, and 99.7%, respectively. PPGs were Fluka products with the exception of PPG 725, which was purchased from Aldrich. Their stated purities were $\geq 99\%$. All chemicals were used without further purification. To reduce the water content, substances were kept over freshly activated molecular sieves (Union Carbide, type 4A) for several days, protected from atmosphere and carbon dioxide. Before measurements, pure liquids were de-

gassed by ultrasound (ultrasonic bath, Hellma, type 460, Milan, Italy) and stored in dark bottles. The molecular weights and molecular mass distributions of PPGs were obtained by the MALDI–TOF mass spectrometric analysis. Data on MALDI–TOF measurements for these samples have been already published [9]. These experiments allowed to compute 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, where N_i is the number of moles of species i , having molecular weight M_i , and mass fraction w_i . A polydispersity index was obtained as the ratio M_w/M_n . Table 1 reports molecular weights and polydispersity indices of the polymers investigated in this work. Experimental densities, ρ , of pure components were determined by a vibrating tube density meter (Anton Paar, model 60/602, Graz, Austria). The measured values are reported in Table 1, together with comparisons to literature data [10–12].

2.2. Calorimetric measurements

The flow-microcalorimeter from LKB (model 2107, Bromma, Sweden) used for the experiments and the experimental procedure were described elsewhere [13,14]. The chemicals were pumped into the mixing cell of the calorimeter by two automatic burettes (ABU, Radiometer, Copenhagen, Denmark). The temperature of the apparatus was kept constant to ± 0.01 K and mass fractions, w_1 , of PEGs were determined by flow rates that were selected to cover the whole mass fraction range. In most cases, the total flow rate was $0.5 \text{ cm}^3 \text{ min}^{-1}$. A few measurements were carried out at a total flow rate of $0.2 \text{ cm}^3 \text{ min}^{-1}$. Over most of the composition range uncertainties in H^E , and in the mass fractions of PPGs are estimated to be less than 1% and 2×10^{-4} , respectively. Miscibility of the components was tested prior to measurements. The calorimeter was checked using the mixture cyclohexane + hexane, whose excess enthalpies are well known in the literature [15]. Agreement between literature data and ours was better than 0.5% over the central range of the mole fraction of cyclohexane.

3. Results and discussion

The measured excess enthalpies, H^E , of PPGs + benzyl alcohol, or + *m*-cresol, or + anisole at 308.15 K and at atmo-

Table 1
Molecular weights, polydispersity indexes and densities, ρ , of pure chemicals and comparison with literature at 308.15 K

Component	M_w	M_w/M_n	Monomer average units	ρ (g cm^{-3})	
				Experimental	Literature
PPG 400	512	1.02	8	0.99568	
PPG 725	884	1.03	14	0.99353	
PPG 1200	1374	1.03	22	0.99303	
PPG 2000	2063	1.03	34	0.99212	
Benzyl alcohol				1.03370	1.0329 [10]
<i>m</i> -Cresol				1.02200	1.022 [11]
Anisole				0.97978	0.9798 [12]

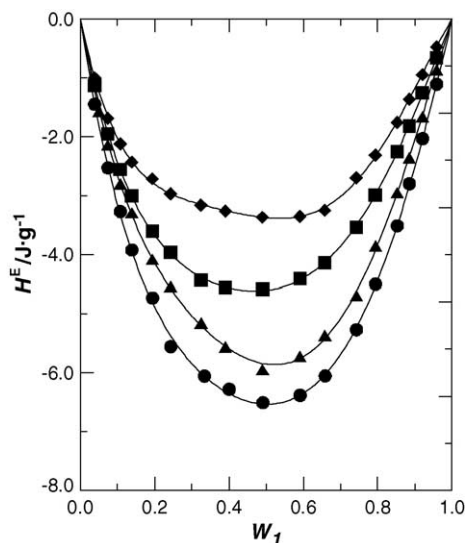


Fig. 1. Excess enthalpies, H^E , of binary mixtures containing PPG 400 (1) (●), PPG 725 (1) (▲), PPG 1200 (1) (■), or PPG 2000 (1) (◆) + benzyl alcohol (2) at 308.15 K. Full lines correspond to the Redlich–Kister polynomial.

spheric pressure are listed in Table 2 and plotted in Figs. 1–3. Polydispersity of PPG samples led to prefer the use of the polymer mass fraction, w_1 , as the independent coordinate. In fact, for polydisperse samples, molecular weights are defined as averages, and the polymer molar fractions will correspond to average numbers of molecules in the solution. Thus, the use of molar fractions may prove misleading, particularly when effects of large molecular weight tails are significant.

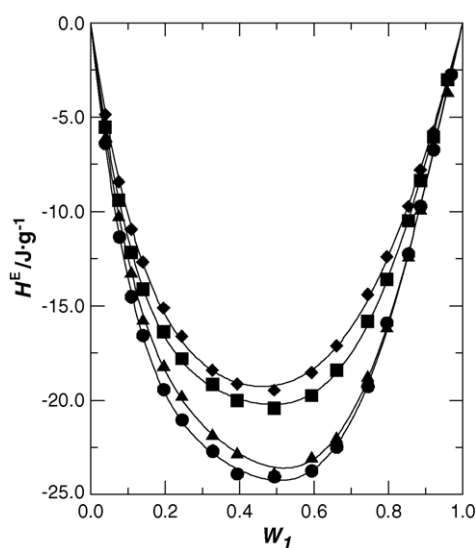


Fig. 2. Excess enthalpies, H^E , of binary mixtures containing PPG 400 (1) (●), PPG 725 (1) (▲), PPG 1200 (1) (■), or PPG 2000 (1) (◆) + *m*-cresol (2) at 308.15 K. Full lines correspond to the Redlich–Kister polynomial.

Table 2
Excess molar enthalpies, H^E , of binary mixtures at 308.15 K^a

w_1	H^E (J g ⁻¹)	w_1	H^E (J g ⁻¹)	w_1	H^E (J g ⁻¹)
PPG 400 + benzyl alcohol					
0.0386	-1.4512	0.3338	-6.0587	0.7940	-4.5000
0.0743	-2.5309	0.4003	-6.2828	0.8525	-3.5141
0.1075	-3.2720	0.4907	-6.5090	0.8851	-2.8003
0.1383	-3.9264	0.5911	-6.3842	0.9204	-2.0345
0.1941	-4.7332	0.6583	-6.0549	0.9585	-1.1108
0.2431	-5.5570	0.7429	-5.2713		
PPG 725 + benzyl alcohol					
0.0501	-1.5703	0.3246	-5.1556	0.7936	-3.8561
0.0741	-2.1438	0.3904	-5.5623	0.8522	-2.9500
0.1073	-2.8024	0.4901	-5.9504	0.8849	-2.3624
0.1381	-3.2949	0.5905	-5.7229	0.9202	-1.6612
0.1937	-4.0821	0.6578	-5.3709	0.9584	-0.8631
0.2426	-4.5440	0.7425	-4.6936		
PPG 1200 + benzyl alcohol					
0.0385	-1.1325	0.3245	-4.4363	0.7935	-2.9881
0.0741	-1.9561	0.3903	-4.5584	0.8522	-2.2512
0.1072	-2.5543	0.4900	-4.5881	0.8849	-1.8214
0.1380	-3.0051	0.5904	-4.4031	0.9202	-1.2524
0.1937	-3.6084	0.6577	-4.1422	0.9584	-0.6567
0.2425	-3.9625	0.7424	-3.5367		
PPG 2000 + benzyl alcohol					
0.0384	-1.0001	0.3243	-3.1648	0.7934	-2.3132
0.0740	-1.6877	0.3901	-3.2617	0.8521	-1.7565
0.1071	-2.1203	0.4897	-3.3701	0.8848	-1.3700
0.1379	-2.4326	0.5902	-3.3536	0.9201	-0.9478
0.1935	-2.7154	0.6575	-3.2496	0.9584	-0.4746
0.2424	-2.9728	0.7422	-2.7011		
PPG 400 + <i>m</i> -cresol					
0.0390	-6.4001	0.3276	-22.7067	0.7958	-15.9040
0.0771	-11.3675	0.3937	-23.9142	0.8540	-12.2612
0.1086	-14.5166	0.4935	-24.0542	0.8863	-9.7311
0.1397	-16.5652	0.5938	-23.7458	0.9212	-6.7412
0.1959	-19.4365	0.6609	-22.4902	0.9690	-2.7559
0.2452	-21.0420	0.7451	-19.2771		
PPG 725 + <i>m</i> -cresol					
0.0399	-6.0144	0.3271	-21.8070	0.7954	-16.1036
0.0749	-10.2115	0.3931	-22.7730	0.8537	-12.3613
0.1084	-13.2212	0.4929	-23.8469	0.8861	-9.8615
0.1394	-15.6891	0.5933	-23.0024	0.9211	-6.5422
0.1955	-18.1268	0.6604	-21.9621	0.9589	-3.6326
0.2447	-19.7253	0.7447	-18.7092		
PPG 1200 + <i>m</i> -cresol					
0.0389	-5.5241	0.3270	-19.1706	0.7954	-13.6144
0.0749	-9.4224	0.3930	-20.0227	0.8536	-10.5000
0.1083	-12.1858	0.4928	-20.4230	0.8860	-8.3600
0.1394	-14.1083	0.5932	-19.7431	0.9211	-6.0502
0.1954	-16.3566	0.6602	-18.4124	0.9589	-3.0249
0.2446	-17.7879	0.7446	-15.8178		
PPG 2000 + <i>m</i> -cresol					
0.0389	-4.8533	0.3268	-18.4001	0.7952	-12.4110
0.0748	-8.4446	0.3928	-19.1242	0.8535	-9.7425
0.1082	-10.9589	0.4926	-19.4638	0.8859	-7.8140
0.1392	-12.7009	0.5930	-18.5314	0.9210	-5.7925
0.1953	-15.1078	0.6600	-17.1122	0.9590	-3.0001
0.2445	-16.6011	0.7444	-14.4000		
PPG 400 + anisole					
0.0406	0.3380	0.3369	0.9832	0.8026	0.4302

Table 2 (Continued)

w_1	H^E (J g ⁻¹)	w_1	H^E (J g ⁻¹)	w_1	H^E (J g ⁻¹)
0.0781	0.5660	0.4038	0.9636	0.8591	0.3021
0.1127	0.7212	0.5041	0.8792	0.8905	0.2417
0.1448	0.8243	0.6040	0.7736	0.9242	0.1541
0.2026	0.9285	0.6703	0.6693	0.9606	0.0740
0.2530	0.9576	0.7530	0.5335		
PPG 725 + anisole					
0.0405	0.1253	0.3364	-0.2633	0.8022	-0.1880
0.0779	0.1605	0.4033	-0.3319	0.8589	-0.1727
0.1125	0.1496	0.5035	-0.3487	0.8903	-0.1584
0.1446	0.1034	0.6034	-0.2948	0.9116	-0.1441
0.2022	-0.0089	0.6698	-0.2488	0.9605	-0.0856
0.2526	-0.1157	0.7526	-0.2081		
PPG 1200 + anisole					
0.0405	-0.0373	0.3363	-0.7870	0.8021	-0.5143
0.0779	-0.1143	0.4031	-0.8709	0.8588	-0.4000
0.1124	-0.2064	0.5034	-0.8770	0.8902	-0.3333
0.1445	-0.3029	0.6033	-0.7723	0.9240	-0.2467
0.2022	-0.4785	0.6696	-0.7088	0.9605	-0.1500
0.2525	-0.6248	0.7525	-0.5840		
PPG 2000 + anisole					
0.0405	-0.0414	0.3361	-0.9818	0.8020	-0.6685
0.0778	-0.1341	0.4029	-1.0587	0.8587	-0.5280
0.1124	-0.2450	0.5031	-1.1132	0.8901	-0.4188
0.1444	-0.3665	0.6031	-1.0009	0.9240	-0.3213
0.2020	-0.5821	0.6694	-0.9332	0.9605	-0.1776
0.2523	-0.7577	0.7523	-0.7663		

^a Poly(propylene glycols) are labelled as component 1.

Values of H^E in Table 2 were fitted to the Redlich–Kister polynomial [16]:

$$H^E = w_1 w_2 \sum_{k \geq 0} a_k (w_1 - w_2)^k \quad (1)$$

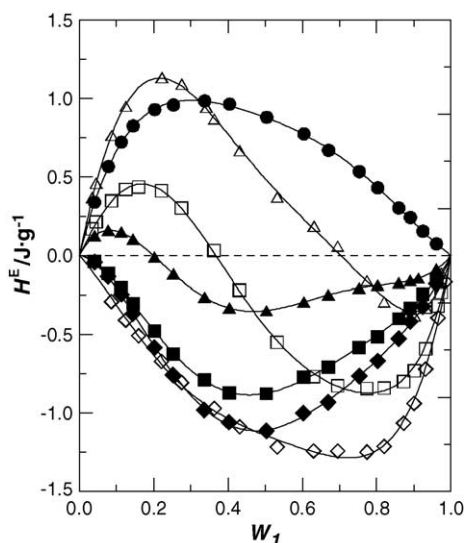


Fig. 3. Excess enthalpies, H^E , of binary mixtures containing PPG 400 (1) (●), PPG 725 (1) (▲), PPG 1200 (1) (■), PPG 2000 (1) (◆), PEG 400 (1) (△) [18], PEG 400 (1) (□) [18] or PEG 600 (1) (◇) [18] + anisole (2) at 308.15 K. Full lines correspond to the Redlich–Kister polynomial.

by a method of unweighted least-squares, where w_1 and w_2 are the mass fractions of PPG and cyclic compounds, respectively, and a_k are the adjustable parameters. Values of a_k are reported in Table 3, together with the standard deviation $\sigma(H^E)$, defined as

$$\sigma(H^E) = [\phi_{\min}/(N - n)]^{1/2} \quad (2)$$

In the above equation, N and n are the number of experimental points and of adjustable parameters respectively and ϕ_{\min} is the minimum value of the objective function ϕ defined as

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

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

Plots in Figs. 1 and 2 show that, for mixtures with benzyl alcohol and *m*-cresol, H^E is negative in the whole composition range and increases as the molecular weight of the polymer is increased. Curves are symmetrical and minima are at $w_1 \cong 0.5$. Such analogies suggest that the trends reported in these Figures may stem from similar types of interactions between the components. At a first approximation, H^E can be assumed proportional to $E_{11} + E_{22} - 2E_{12}$, where E_{ij} is the interaction energy between molecules of types i and j . Thus, negative values of H^E correspond to $2E_{12} > E_{11} + E_{22}$. Figs. 1 and 2 show that $2E_{12}$ (the energy associated to heteromolecular interactions) is larger for the *m*-cresol mixtures. Moreover, *m*-cresol and benzyl alcohol mixtures display systematic changes of H^E with the polymer molecular mass. At constant values of w_1 , these trends might be related to the decrease of the contribution of heteromolecular interactions as the length of the polymer chain is increased.

Mixtures of PPG + anisole display more complex trends (Fig. 3). The effects of changes in the polymer molecular weight are more significant. Actually, as M_w of the polymer is increased, H^E changes from completely positive values to an inversion of sign and down to negative values in the whole composition range. Plots in Fig. 3 show that changes in H^E are smaller, $\sim 2 \text{ J g}^{-1}$ in the whole composition range, a fact which might be related to the increasing fraction of weak H-bonds ($-\text{C}-\text{H} \cdots \text{O}$) [17] between methylene groups and etheric O atoms, replacing the stronger hydroxyl–hydroxyl interactions with alcohols.

Fig. 3 reports also data obtained on mixtures of poly(ethylene glycols) (PEG) + anisole [18]. Comparisons with PPG curves can provide information on the effects of the addition of the $-\text{CH}_3$ hydrophobic group to the polymer chain. As reported in Table 4, PEG 400 and PPG 400 have the same number of monomer units in the chain. Such a number is similar for PEG 600 and PPG 725 samples too. Moreover, values of M_w and M_n of PEG 600 are close to the corresponding values of PPG 400. Plots in Fig. 3 show that three mixtures of PEGs + anisole display trends that, for $w_1 < 0.5$, are similar to those of the PPG mixtures with H^E values of the same

Table 3

Least-squares parameters, a_k (J g^{-1}), Eq. (1), and standard deviations, $\sigma(H^E)$, Eq. (2), for binary mixtures containing poly(propylene glycols) (1) + benzyl alcohol (2), or + *m*-cresol (2), or + anisole (2) at 308.15 K

Mixture	a_0	a_1	a_2	a_3	$\sigma(H^E)$ (J g^{-1})
PPG 400 + benzyl alcohol	-26.132	-0.25078	-8.3402	7.3943	0.065
PPG 725 + benzyl alcohol	-23.418	-1.7713	-4.2050	9.4249	0.051
PPG 1200 + benzyl alcohol	-18.431	1.4621	-6.0325	6.9730	0.024
PPG 2000 + benzyl alcohol	-13.509	-1.2214	-6.6709	11.108	0.032
PPG 400 + <i>m</i> -cresol	-97.007	-1.6730	-40.221	57.361	0.18
PPG 725 + <i>m</i> -cresol	-94.300	-4.5445	-35.673	50.031	0.18
PPG 1200 + <i>m</i> -cresol	-80.870	1.9837	-36.989	41.194	0.14
PPG 2000 + <i>m</i> -cresol	-76.775	7.3395	-28.503	24.540	0.19
PPG 400 + anisole	3.5186	-1.7734	2.0933	-2.1746	0.008
PPG 725 + anisole	-1.3965	0.51670	2.2115	-4.1519	0.001
PPG 1200 + anisole	-3.5013	0.86489	1.2348	-2.8910	0.007
PPG 2000 + anisole	-4.4340	0.62596	1.6169	-3.0837	0.011

order of magnitude. Such a composition range corresponds to a region where the most probable interactions are of types 1-1 and 1-2 and all polymer molecules are likely involved in heteromolecular interactions. When polymer–polymer interactions become more probable ($w_1 > 0.5$), differences in the chain structures of PPG and PEG introduce significant displacements in the corresponding trends in Fig. 3. A global inspection of data in this Figure shows that similar numbers of monomer units between PEG 400 and PPG 400 and between PEG 600 and PPG 725 do not correspond to similar H^E curves. Such a correspondence is shifted towards PPG samples of larger M_w so that the curve of PEG 600 lies closer to the PPG 1200 and PPG 2000 curves.

An attempt can be made to interpret trends in Figs. 1–3 by the regular solution model, assuming that mixing of the two species is random and is not affected either by differences in molecular sizes or by preferential energetics. In this model $H^E \cong a_0 w_1 w_2$, where $a_0 \propto E_{11} + E_{22} - 2E_{12}$, and ex-

perimental values of $H^E/w_1 w_2$ for $w_1 \rightarrow 0$ and $w_1 \rightarrow 1$ should both be equal to a_0 and independent of j , the number of monomer units in the polymer chain [9]. Data reported in Table 4 does not seem consistent with this model. However, a closer inspection shows that, for mixtures with benzyl alcohol and *m*-cresol, values of $H^E/w_1 w_2$ extrapolated at $w_1 \rightarrow 0$ are almost twice the corresponding values obtained at $w_1 \rightarrow 1$. Thus, the regular solution model can be applied to these mixtures under the assumption that, at small polymer concentrations, each polymer molecule interacts with two alcohol molecules via its two hydroxyl end-groups. Under this assumption, as reported in Fig. 4, the regular solution model is consistent with the behavior of alcohol mixtures.

In contrast, plots in Fig. 3 and data in Table 4 confirm that both PEG and PPG mixtures with anisole deviate from the regular solution model. It can be noted that for PPG mixtures such deviations are more significant in the range of small polymer mass fractions.

Table 4

Analysis of the consistency of the regular solution model for PPG and PEG mixtures

Mixture	Monomer average units	a_0	$\lim_{w_1 \rightarrow 1}(H^E/w_1 w_2)$	$\lim_{w_1 \rightarrow 0}(H^E/w_1 w_2)$
PPG 400 + benzyl alcohol	8	-26.132	-27.330	-41.614
PPG 725 + benzyl alcohol	14	-23.418	-19.971	-35.274
PPG 1200 + benzyl alcohol	22	-18.431	-16.030	-32.897
PPG 2000 + benzyl alcohol	34	-13.509	-10.295	-30.063
PPG 400 + <i>m</i> -cresol	8	-97.007	-81.549	-192.90
PPG 725 + <i>m</i> -cresol	14	-94.300	-84.494	-175.45
PPG 1200 + <i>m</i> -cresol	22	-80.870	-74.687	-161.03
PPG 2000 + <i>m</i> -cresol	34	-76.775	-73.401	-137.15
PPG 400 + anisole	8	3.5186	1.6642	9.5593
PPG 725 + anisole	14	-1.3965	-2.8195	4.4491
PPG 1200 + anisole	22	-3.5013	-4.2921	-0.24108
PPG 2000 + anisole	34	-4.4340	-5.2743	-0.36016
PEG 200 + anisole [18]	3	6.6732	-2.1421	29.986
PEG 300 + anisole [18]	5	2.1507	-6.6612	13.347
PEG 400 + anisole [18]	8	-1.8044	-11.8967	4.9245
PEG 600 + anisole [18]	12	-4.5692	-13.6254	-2.6171

The first parameter, a_0 , of the Redlich–Kister polynomial is compared to extrapolations from data in Table 2.

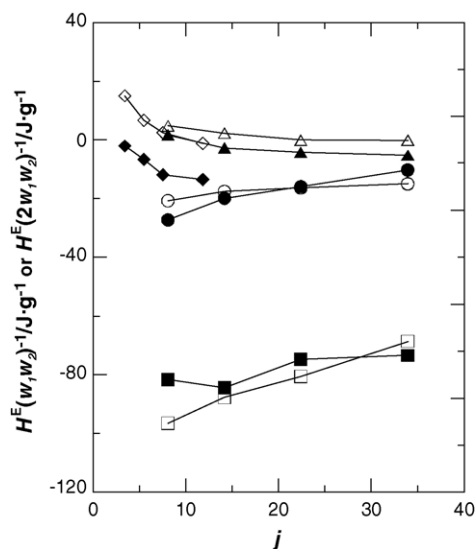


Fig. 4. Values of H^E/w_1w_2 at $w_1 \rightarrow 1$ (filled symbols) and $H^E/2w_1w_2$ at $w_1 \rightarrow 0$ (open symbols) vs. the average number of monomer units, j ; (●, ○) PPG + benzyl alcohol; (■, □) PPG + *m*-cresol; (▲, △) PPG + anisole; (◆, ◇) PEG + anisole.

4. Conclusions

Investigations on the excess enthalpies of mixing of PPG samples of different molecular weight showed that mixtures with anisole behave quite differently from mixtures with benzyl alcohol and *m*-cresol. These last two compounds can interact with PPG molecules via strong H-bonds involving the $-OH$ groups of both mixture components. Moreover, for these two types of mixtures, the limiting trends of H^E for $w_1 \rightarrow 0$ and $w_1 \rightarrow 1$ follow patterns corresponding to the regular solution model, provided that account is taken of the two hydroxyl end-groups per molecule in the polymer chain. In contrast, PPG mixtures with anisole do not seem consistent with this model; values of H^E follow more complex patterns as the composition of the mixture is changed.

For PPGs of low molecular weight, Fig. 3 reports positive deviations or inversions of sign in H^E . This suggests that, for these mixtures, homomolecular interactions, via $-OH$ end-groups of two different PPG molecules, are more significant.

In fact, for shorter chains, $-OH$ end groups are not yet outnumbered by the etheric O atoms as in polymer samples of higher molecular weight.

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