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Excess Enthalpies, Densities, Viscosities, and Refractive Indices of Binary Mixtures Involving Some Poly(glycols) + Diethyl Carbonate at 308.15 K

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Densities, viscosities, refractive indices, and excess enthalpies have been measured at 308.15 K and at atmospheric pressure for poly(ethylene glycols) 200, 400, and 600 and poly(propylene glycols) 400, 725, and 2000 + diethyl carbonate over the whole composition range. Enthalpy values are all positive, while volumetric values are negative with the exception of the mixture containing poly(propylene glycol) 400, where an inversion of sign is observed. Viscosity deviations are negative for all mixtures. Viscosities and viscosity deviations display complex dependencies on the type of polymer and on its molecular mass. The experimental results were fitted to the Redlich−Kister polynomial. The results are qualitatively discussed in terms of molecular interactions.

Introduction

Poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) are polyethers whose chains are made of oxyethylene, $-[CH_2CH_2O]-$, and oxypropylene, $-[CH_2CH(CH_3)O]-$, units, respectively, terminated by hydroxyl groups at both ends. The presence of both hydrophobic and hydrophilic groups may account for the ability of these polymers to dissolve in a large number of substances as well as for their complex solution behavior. Competition between hydrophobic and hydrophilic interactions has been invoked to explain changes in the conformation of PEG molecules in solution.[1,2] Moreover, the molecular mass of the polymer seems to control its conformation in aqueous solution. PEG of high molecular mass retains the helical conformation of the crystalline state, with the hydrocarbon groups inside the helix, whereas low molecular mass PEG displays random coil conformation.[1] As a water-soluble polymer, PEG is widely used in the petroleum, cosmetic, and food industry.[3] Its applications range from use as a polymer electrolyte to treatment of surfaces for protein absorption resistance.[4−6]

Studies on PPG have mostly focused on its molecular glassformer nature. In fact, the methyl group prevents crystallization of the undercooled liquid;[7] thus, special attention has been devoted to the dynamics of this group as the system temperature approaches the glass transition temperature, T_g.[8,9] Aqueous solutions of PPG and its copolymers have been extensively studied due to the variety of their phase behavior. For PPG, changes in molecular conformation, from random coil (nonpolar) to helical (polar), are detected upon dissolution in polar solvents, like water.[10] In contrast to PEG, PPG is only partially soluble in water. The additional hydrophobic effect of the methylene group should account for most of the differences in the solution properties of PEG and PPG. In fact, the solution behavior of these polymers stems from a complex combination of conformational and energetic effects and of the corresponding changes in the H-bond patterns governing molecular interactions in solutions.

This work is a continuation of our systematic research program concerning the study of the physical and bulk properties of binary mixtures containing poly(glycols).[11−13] This paper reports experimental densities, ρ, dynamic viscosities, η, refractive indices, n_D, and excess enthalpies, H^E, of binary mixtures of some PEGs and PPGs + diethyl carbonate at 308.15 K and at atmospheric pressure. Diethyl carbonate is an aprotic solvent, used in several extraction processes, in the synthesis of pharmaceuticals, and in agricultural chemistry.[14−16] On mixing, ester molecules should perturb the network of inter- and intramolecular H bonds in the polymer. Previous investigations on similar mixtures showed that the degree of interaction between the components depends on the molar mass of the polymer.[17,18] It is the aim of the present work to investigate further this correlation and to study possible changes in the interactions between diethyl carbonate and the polymer chain by the influence of the methylene group in the PPG molecules.

Poly(glycols) investigated in this work are poly(ethylene glycols), PEG 200, PEG 400, and PEG 600, and poly(propylene glycols), PPG 400, PPG 725, and PPG 2000. A literature survey showed that no measurements have been previously reported for the mixtures studied in this work.

Experimental Section

Chemicals. Chemicals used in this work were obtained from Fluka, except for PPG 725 and diethyl carbonate, purchased from Aldrich. Substances were analytical grade, with purities ≥ 99%. Substances were kept over freshly activated molecular sieves (Union Carbide type 4A) for several days before use, to reduce the water content, and were protected from atmospheric moisture and carbon dioxide. After this treatment, the content of water, as determined by gas−liquid chromatography analysis, was ≤0.01 mass%. Before use, pure liquids were also degassed by ultrasound (ultrasonic bath, Hellma, type 460, Milan, Italy).

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Table 1. Densities, ρ, Dynamic Viscosities, η, and Refractive Indices, n_D, of Pure Components at 308.15 K and Comparison with Literature Values

				ρ/g·cm^{-3}		η/mPa·s		n_D	
compound	M_n	M_w	M_w/M_n	this work	lit	this work	lit	this work	lit
PEG 200	184	204	1.108	1.11300	1.11243[a]	30.03	28.066[a]	1.4554	
PEG 400	365	401	1.098	1.11437	1.11372[b]	55.84		1.4620	
PEG 600	554	587	1.06	1.11440		84.04		1.4638	
PPG 400	502	512	1.02	0.99580		39.50		1.4429	
PPG 725	856	884	1.03	0.99361		65.61		1.4446	
PPG 2000	2004	2063	1.03	0.99215		186.9		1.4461	
Diethyl Carbonate				0.95790	0.9579[c]	0.662		1.3781	1.37769[c]

[a] Reference 28. [b] Reference 29. [c] Reference 30

The molecular weights of PEGs were obtained by gel permeation chromatography (GPC) and by Electrospray (ESI) mass spectrometric analysis. For PPGs, it was possible to use the matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) technique to measure molecular weights and molecular mass distributions. Detailed results of the GPC[12,17] and MALDI-TOF[19] measurements for these samples have been already published. Both methods allowed us to compute the number average, M_n ($\Sigma N_i M_i/\Sigma N_i$), and the weight average, M_w ($\Sigma N_i M_i^2/\Sigma N_i M_i = \Sigma w_i M_i$), 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 the polydispersity index of the polymers investigated in this work. Concentrations of the components in the binary mixtures are given in mass fractions, because polydispersities of the polymer samples lead to uncertainties in the evaluation of the corresponding mole fractions. Thus, excess enthalpies, H^E, and excess volumes, V^E, are expressed as J·g^{-1} and cm^3·g^{-1}, respectively. For the same reason, we did not report molar refractions, performing direct comparisons on refractive indices.

Calorimetric Measurements. The excess enthalpies, H^E, were measured by a flow isothermal microcalorimeter (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 burets (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 mass fractions in the mixed stream were calculated from densities and volumetric flow rates of components 1 (PEGs or PPGs) and 2 (diethyl carbonate). The total flow rates are usually kept at about 0.4 cm^3·min^{-1}, but in dilute regions, the total flow rates may increase up to 0.8 cm^3·min^{-1}. Details and operating procedures of the apparatus have been reported elsewhere.[20,21] The accuracy of the reported H^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.[22] Agreement with literature data is better than 0.5% at the maximum of the thermal effect.

Density Measurements. Mixtures were prepared by mass in airtight-stoppered bottles, using a digital balance (Mettler, model AE 160, Switzerland), covering the whole mass fraction range. The whole procedure was described elsewhere.[23] Densities of the liquids were measured by means of a vibrating tube density meter (Anton Paar, model DMA 60/602), Graz, Austria). The temperature inside the vibrating-tube cell was measured by a digital thermometer (Anton Paar, type CTK 100) and was regulated to better than ±0.01 K using a water circulating bath (Heto, type 01 DBT 623, Birkeròd, Denmark). Before each series of measurements, the apparatus was calibrated at atmospheric pressure using double-distilled water and dry air, whose densities were taken from the literature.[24,25] The uncertainty in the densities was $\pm 1.5 \times 10^{-5}$ g·cm^{-3} at 308.15 K. Correspondingly, the uncertainty in V^E is estimated as <1%. Before measurements, the apparatus was checked by determining the excess molar volume, V_m^E, using the test mixture benzene + cyclohexane at 298.15 K. Agreement of our results with those of literature[26] is within 1%.

Viscosity Measurements. The kinematic viscosities, ν, were determined using several Ubbelohde viscometers, according to the equation

$$\nu = \eta/\rho = k(t - \theta) \qquad (1)$$

where η is the dynamic viscosity, ρ is the density, t is the flow time, θ is the kinetic energy correction, and k is the viscometer constant, determined by calibration. Flow times were measured by a Schott-Geräte automatic measuring unit (model AVS 350), equipped with a thermostat (Lauda, model E 200, Germany), providing temperature stabilization with an accuracy of ±0.01 K. Several viscometers with capillary diameters from 0.47 mm up to 1.50 mm were used for kinematic ranges of (0.69 to 189) mm^2·s^{-1}. Viscometer calibration was performed by double-distilled water and by a standard oil specimen of known viscosity, provided by Haake. Viscometers were filled with 15 cm^3 of solution, and the flow times were obtained by averaging over six runs. Flow times were always >200 s, by selecting an appropriate viscometer. The uncertainty of the viscosity measurements was ±0.5%.

Refractive Indices. Refractive indices, n_D, at the sodium line, were measured to within ±0.0001 by an Abbe refractometer (Carl Zeiss, model G, Jena, Switzerland). The refractometer was calibrated using distilled water, in accordance with the instrument instructions. Water was circulated into the instrument through a thermostatically controlled bath, whose temperature stability was ±0.05 K. The refractive index measurements were performed after the liquid mixtures attained a constant temperature in the refractometer cell, as measured by a control thermometer. The procedure was repeated at least five times, and the refractive index was taken as the average of these measurements.

Table 1 reports measured values of ρ, η, and n_D of the pure liquids together with comparisons to literature data.

Results and Discussion

Excess enthalpies, H^E (J·g^{-1}), for binary mixtures of PEGs or PPGs with diethyl carbonate are reported in Table

Table 2. Excess Enthalpies, H^E, for Binary Mixtures Containing PEG or PPG + Diethyl Carbonate 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}
		PEG 200 (1) + Diethyl Carbonate (2)			
0.0462	2.2500	0.3675	6.2221	0.8229	3.4827
0.0883	3.7604	0.4364	5.9893	0.8746	2.7554
0.1285	4.7847	0.5374	5.5006	0.9029	2.1865
0.1622	5.3326	0.6355	4.8860	0.9331	1.6892
0.2251	6.0421	0.6991	4.5453	0.9654	0.8982
0.2792	6.2517	0.7771	3.9002		
		PEG 400 (1) + Diethyl Carbonate (2)			
0.0462	1.2924	0.3677	4.0903	0.8231	2.3508
0.0883	2.2705	0.4366	4.0021	0.8747	1.7339
0.1269	2.8784	0.5377	3.7017	0.9030	1.4958
0.1624	3.2769	0.6357	3.3699	0.9332	1.0972
0.2253	3.7787	0.6994	3.0450	0.9654	0.6151
0.2794	3.9915	0.7773	2.6312		
		PEG 600 (1) + Diethyl Carbonate (2)			
0.0462	0.9125	0.3678	2.7635	0.8231	1.6332
0.0884	1.5337	0.4367	2.6968	0.8747	1.2845
0.1270	1.9289	0.5378	2.5771	0.9030	1.0263
0.1624	2.1967	0.6358	2.3642	0.9332	0.7187
0.2253	2.5003	0.6994	2.1708	0.9614	0.4500
0.2794	2.6669	0.7773	1.8881		
		PPG 400 (1) + Diethyl Carbonate (2)			
0.0415	0.6598	0.3420	3.1071	0.8061	2.0384
0.0797	1.2068	0.4093	3.2146	0.8618	1.6397
0.1150	1.5763	0.5097	3.1355	0.8927	1.3887
0.1477	1.8907	0.6094	2.9043	0.9258	1.0070
0.2063	2.3938	0.6752	2.6971	0.9615	0.5801
0.2573	2.8241	0.7572	2.3037		
		PPG 725 (1) + Diethyl Carbonate (2)			
0.0414	0.3214	0.3415	1.5007	0.8057	1.1336
0.0795	0.5785	0.4087	1.5643	0.8615	0.9080
0.1148	0.7752	0.5091	1.6058	0.8924	0.7500
0.1474	0.9317	0.6088	1.5630	0.9256	0.5268
0.2059	1.1628	0.6747	1.4741	0.9614	0.3099
0.2569	1.3520	0.7568	1.2958		
		PPG 2000 (1) + Diethyl Carbonate (2)			
0.0414	0.0997	0.3412	0.4447	0.8056	0.4412
0.0794	0.1662	0.4084	0.4784	0.8614	0.3681
0.1146	0.2261	0.5088	0.5166	0.8923	0.3142
0.1472	0.2656	0.6085	0.5315	0.9255	0.2379
0.2057	0.3385	0.6744	0.5221	0.9613	0.1369
0.2566	0.3855	0.7565	0.4829		

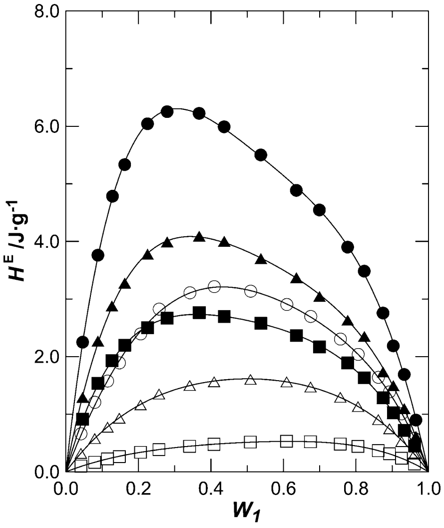

Figure 1. Excess enthalpies, H^E, vs the mass fraction, w_1, of PEGs (filled symbols) or PPGs (open symbols) + diethyl carbonate at 308.15K. ●, PEG 200; ▲, PEG 400; ■, PEG 600; ○, PPG 400; △, PPG 725; □, PPG 2000. Full lines correspond to the Redlich−Kister polynomial.

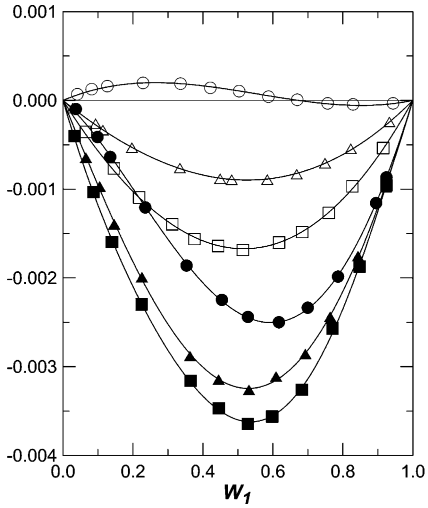

Figure 2. Excess volumes, V^E, vs the mass fraction, w_1, of PEGs (filled symbols) or PPGs (open symbols) + diethyl carbonate at 308.15K. ●, PEG 200; ▲, PEG 400; ■, PEG 600; ○, PPG 400; △, PPG 725; □, PPG 2000. Full lines correspond to the Redlich−Kister polynomial.

2 and Figure 1. Values of H^E are all positive with mixtures of PEG 200 and PEG 400 consistently above the others. For PEG mixtures, maxima are in the w_1 range (0.3 to 0.4). Curves of PPG mixtures are more symmetrical, with maxima at $w_1 \approx 0.5$.

Excess volumes, V^E (cm^3·g^{-1}), were obtained by the following equation

$$V^E = 1/\rho - w_1/\rho_1 - w_2/\rho_2 \qquad (2)$$

where ρ is the density of the mixture and w_i and ρ_i ($i = 1, 2$) are the mass fractions and densities of the ith component, respectively. The corresponding values are reported in Table 3 and Figure 2. Plots of V^E in Figure 2 show that excess volumes are negative in the whole composition range with the exception of the PPG 400 mixture, which displays an inversion of sign. Negative values of V^E suggest that molecular packing of diethyl carbonate with polymeric chains is more efficient than homomolecular packing.

The deviations in viscosity, $\Delta\eta$, were calculated from the definition

$$\Delta\eta = \eta - (w_1\eta_1 + w_2\eta_2) \qquad (3)$$

where η, η_1, and η_2 are the viscosities of the mixture and of pure components, respectively. Values of $\Delta\eta$ are reported in Table 3 and plotted in Figure 3 against the mass fraction of the polymers. The uncertainty of the viscosity deviations was ±1.5%. It can be seen that $\Delta\eta$ is negative for all the investigated binary systems, over the whole composition range. Minima are located at $w_1 \approx 0.7$ to 0.8. Table 4 reports the refractive indices, n_D, of the binary mixtures. In Figure 4, plots of n_D show linear dependences on the mass fraction of the polymer. Values of n_D are rather similar, with lines corresponding to PEG mixtures consistently above the mixtures of PPGs. For a given polymer, n_D of its mixtures increases as the molecular mass of the polymer is increased.

Changes in H^E, V^E, and $\Delta\eta$ with composition can be expressed by the Redlich−Kister equation[27]

$$Q^E_{\text{calc}} = w_1 w_2 \sum_{k\geq 0} a_k (w_1 - w_2)^k \qquad (4)$$

where Q^E_{calc} refers to H^E, V^E, or $\Delta\eta$. The adjustable

Table 3. Densities, ρ, Excess Volumes, V^E, Dynamic Viscosities, η, and Viscosity Deviations, $\Delta\eta$, for Mixtures of PEG or PPG + Diethyl Carbonate at 308.15 K

w_1	ρ/g·cm^{-3}	V^E/cm^3·g^{-1}	η/mPa·s	$\Delta\eta$/mPa·s	w_1	ρ/g·cm^{-3}	V^E/cm^3·g^{-1}	η/mPa·s	$\Delta\eta$/mPa·s
				PEG 200 (1) + Diethyl Carbonate (2)					
0.0366	0.96268	−0.0001	0.713	−1.02	0.5285	1.03657	−0.0024	3.624	−12.6
0.0984	0.97140	−0.0004	0.830	−2.72	0.6172	1.05071	−0.0025	5.149	−13.6
0.1348	0.97664	−0.0006	0.917	−3.70	0.6996	1.06396	−0.0023	7.280	−13.9
0.2351	0.99135	−0.0012	1.244	−6.32	0.7861	1.07803	−0.0020	10.69	−13.1
0.3531	1.00922	−0.0019	1.878	−9.16	0.8951	1.09581	−0.0012	17.84	−9.11
0.4542	1.02486	−0.0022	2.801	−11.2	0.9246	1.10065	−0.0009	20.62	−7.20
				PEG 400 (1) + Diethyl Carbonate (2)					
0.0653	0.96721	−0.0006	0.801	−3.46	0.5315	1.03847	−0.0033	4.964	−25.0
0.1047	0.97295	−0.0010	0.911	−5.53	0.6090	1.05070	−0.0031	7.037	−27.2
0.1463	0.97917	−0.0014	1.055	−7.68	0.6928	1.06414	−0.0029	10.48	−28.4
0.2254	0.99099	−0.0020	1.413	−11.7	0.7638	1.07557	−0.0024	14.98	−27.8
0.3630	1.01211	−0.0029	2.417	−18.3	0.8432	1.08839	−0.0018	22.82	−24.4
0.4447	1.02481	−0.0031	3.397	−21.8	0.9235	1.10156	−0.0010	35.71	−15.9
				PEG 600 (1) + Diethyl Carbonate (2)					
0.0329	0.96271	−0.0004	0.742	−2.67	0.5282	1.03855	−0.0036	6.137	−38.6
0.0869	0.97069	−0.0010	0.904	−7.00	0.5979	1.04960	−0.0036	8.620	−41.9
0.1397	0.97858	−0.0016	1.109	−11.2	0.6828	1.06314	−0.0033	13.23	−44.4
0.2247	0.99135	−0.0023	1.570	−17.8	0.7705	1.07708	−0.0026	21.11	−43.8
0.3643	1.01277	−0.0032	2.893	−28.1	0.8477	1.08954	−0.0019	32.63	−38.7
0.4454	1.02543	−0.0035	4.182	−33.6	0.9251	1.10207	−0.0010	51.71	−26.1
				PPG 400 (1) + Diethyl Carbonate (2)					
0.0409	0.95933	0.0001	0.729	−1.52	0.5033	0.97651	0.0001	2.756	−17.5
0.0818	0.96077	0.0001	0.812	−3.03	0.5873	0.97976	0.0000	3.854	−19.6
0.1268	0.96239	0.0002	0.877	−4.71	0.6695	0.98294	0.0000	5.500	−21.2
0.2287	0.96613	0.0002	1.141	−8.40	0.7566	0.98633	0.0000	8.425	−21.6
0.3359	0.97013	0.0002	1.556	−12.2	0.8292	0.98916	0.0000	12.54	−20.3
0.4212	0.97337	0.0001	2.055	−15.0	0.9435	0.99361	0.0000	26.06	−11.3
				PPG 725 (1) + Diethyl Carbonate (2)					
0.0274	0.95890	−0.0001	0.721	−1.72	0.4821	0.97563	−0.0009	3.443	−28.5
0.0930	0.96133	−0.0003	0.876	−5.82	0.5840	0.97928	−0.0009	5.321	−33.3
0.1139	0.96213	−0.0003	0.930	−7.13	0.6681	0.98226	−0.0008	7.672	−36.4
0.1969	0.96521	−0.0005	1.220	−12.2	0.7490	0.98508	−0.0007	12.08	−37.2
0.3341	0.97024	−0.0008	1.935	−20.4	0.8226	0.98761	−0.0005	18.53	−35.6
0.4492	0.97444	−0.0009	3.000	−26.8	0.9330	0.99137	−0.0002	38.83	−22.4
				PPG 2000 (1) + Diethyl Carbonate (2)					
0.0652	0.96040	−0.0004	0.922	−11.9	0.5140	0.97681	−0.0017	8.027	−88.3
0.1452	0.96345	−0.0008	1.390	−26.3	0.6174	0.98030	−0.0016	13.81	−102.
0.2175	0.96618	−0.0011	1.927	−39.2	0.6835	0.98248	−0.0015	19.93	−108.
0.3122	0.96966	−0.0014	3.014	−55.8	0.7598	0.98493	−0.0013	31.49	−111.
0.3755	0.97196	−0.0016	4.075	−66.5	0.8270	0.98699	−0.0010	48.95	−106.
0.4430	0.97434	−0.0016	5.636	−77.5	0.9152	0.98968	−0.0005	92.53	−78.5

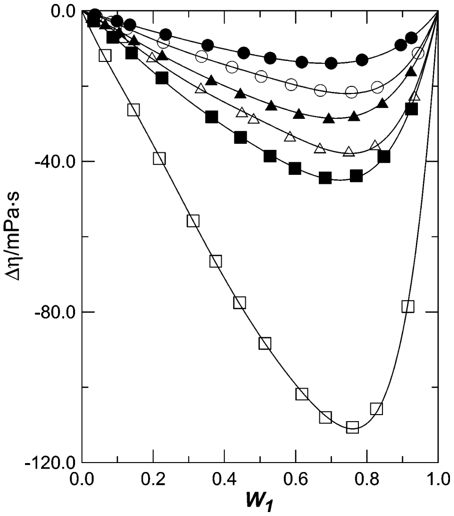

Figure 3. Viscosity deviations, $\Delta\eta$, vs the mass fraction, w_1, of PEGs (full symbols) or PPGs (open symbols) + diethyl carbonate at 308.15K. ●, PEG 200; ▲, PEG 400; ■, PEG 600; ○, PPG 400; △, PPG 725; □, PPG 2000. Full lines correspond to the Redlich−Kister polynomial.

parameters a_k were determined by a least-squares method. The corresponding results are reported in Table 5. The tabulated standard deviations, $\sigma(Q^E)$, reported in the same Table, are defined as

$$\sigma(Q^E) = |\xi_{\min}/(N - n)|^{0.5} \tag{5}$$

with N and n the number of experimental points and of parameters, respectively, whereas $\xi_{\min}$ is the minimum value of the objective function ξ, defined as

$$\xi = \sum_{k=1}^{N} ({Q^E}_{\text{calc}} - Q^E)^2 \tag{6}$$

and Q^E is the experimental value. The full lines in Figures 1−3 correspond to the Redlich−Kister polynomials.

Conclusions

Plots of H^E reported in Figure 1 can be qualitatively explained by assuming that $H^E \propto E_{11} + E_{22} - 2E_{12}$, where E_{ij} is the interaction energy between molecules of type i and j. Thus, positive values of H^E correspond to $E_{11} + E_{22} > 2E_{12}$. This inequality leads to conclude that homomolecular interactions are stronger than heteromolecular interactions, between polymer and diethyl carbonate. Inspection of data in Table 1 and Figure 1 shows that maximum values of H^E for different mixtures depend on

Table 4. Refractive Indices, n_D, for Binary Mixtures Containing PEG or PPG + Diethyl Carbonate at 308.15 K

w_1	n_D	w_1	n_D	w_1	n_D
PEG 200 (1) + Diethyl Carbonate (2)					
0.0366	1.3810	0.3531	1.4039	0.6996	1.4312
0.0984	1.3852	0.4542	1.4117	0.7861	1.4382
0.1348	1.3877	0.5285	1.4174	0.8951	1.4470
0.2351	1.3950	0.6172	1.4245	0.9246	1.4494
PEG 400 (1) + Diethyl Carbonate (2)					
0.0653	1.3833	0.3630	1.4073	0.6928	1.4355
0.1047	1.3863	0.4447	1.4142	0.7638	1.4416
0.1463	1.3897	0.5315	1.4218	0.8432	1.4483
0.2254	1.3960	0.6090	1.4282	0.9235	1.4558
PEG 600 (1) + Diethyl Carbonate (2)					
0.0329	1.3810	0.3643	1.4081	0.6828	1.4360
0.0869	1.3852	0.4454	1.4152	0.7705	1.4438
0.1397	1.3895	0.5282	1.4226	0.8477	1.4508
0.2247	1.3965	0.5979	1.4285	0.9251	1.4576
PPG 400 (1) + Diethyl Carbonate (2)					
0.0409	1.3806	0.3359	1.3991	0.6695	1.4207
0.0818	1.3831	0.4212	1.4046	0.7566	1.4265
0.1268	1.3858	0.5033	1.4100	0.8292	1.4314
0.2287	1.3923	0.5873	1.4154	0.9435	1.4391
PPG 725 (1) + Diethyl Carbonate (2)					
0.0274	1.3799	0.3341	1.4001	0.6681	1.4222
0.0930	1.3841	0.4492	1.4076	0.7490	1.4277
0.1139	1.3855	0.4821	1.4098	0.8226	1.4327
0.1969	1.3910	0.5840	1.4167	0.9330	1.4402
PPG 2000 (1) + Diethyl Carbonate (2)					
0.0652	1.3827	0.3755	1.4037	0.6835	1.4247
0.1452	1.3880	0.4430	1.4082	0.7598	1.4299
0.2175	1.3929	0.5140	1.4134	0.8270	1.4345
0.3122	1.3993	0.6174	1.4203	0.9152	1.4404

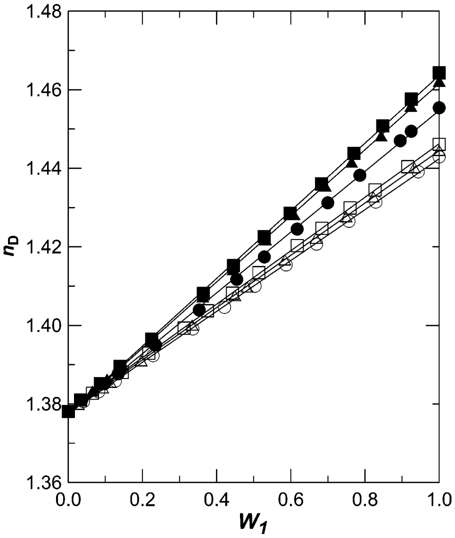

Figure 4. Refractive indices, n_D, vs the mass fraction, w_1, of PEGs (full symbols) or PPGs (open symbols) + diethyl carbonate at 308.15K. ●, PEG 200; ▲, PEG 400; ■, PEG 600; ○, PPG 400; △, PPG 725; □, PPG 2000. Full lines correspond to linear regressions.

Table 5. Adjustable Parameters, a_k, from Equation 4, and Standard Deviations $\sigma(Q^E)$, Equation 5, of PEGs or PPGs + Dialkyl Carbonates at 308.15 K

function	a_0	a_1	a_2	a_3	$\sigma(Q^E)$
PEG 200 (1) + Diethyl Carbonate (2)					
H^E/J·g^{-1}	22.64	−9.876	19.897	−3.762	0.039
V^E/cm^3·g^{-1}	−0.0096	−0.0047	0.0015		1.9 10^{-5}
$\Delta\eta$/mPa·s	−48.17	−33.75	−24.88	−12.85	0.04
PEG 400 (1) + Diethyl Carbonate (2)					
H^E/J·g^{-1}	15.30	−5.606	10.46	−1.251	0.034
V^E/cm^3·g^{-1}	−0.0129	−0.0017	0.0014		2.7 10^{-5}
$\Delta\eta$/mPa·s	−95.21	−71.65	−60.34	−36.85	0.16
PEG 600 (1) + Diethyl Carbonate (2)					
H^E/J·g^{-1}	10.51	−2.647	7.067	−2.328	0.020
V^E/cm^3·g^{-1}	−0.0144	−0.0024	0.0014	0.0030	2.8 10^{-5}
$\Delta\eta$/mPa·s	−146.6	−112.5	−106.7	−74.31	0.44
PPG 400 (1) + Diethyl Carbonate (2)					
H^E/J·g^{-1}	12.64	−2.804	3.729	3.146	0.030
V^E/cm^3·g^{-1}	0.0004	−0.0013			0.9 10^{-5}
$\Delta\eta$/mPa·s	−68.37	−54.81	−61.84	−47.72	0.34
PPG 725 (1) + Diethyl Carbonate (2)					
H^E/J·g^{-1}	6.455	0.0195	2.076		0.011
V^E/cm^3·g^{-1}	−0.0036	−0.0004			0.8 10^{-5}
$\Delta\eta$/mPa·s	−116.1	−93.44	−111.7	−90.98	0.63
PPG 2000 (1) + Diethyl Carbonate (2)					
H^E/J·g^{-1}	2.047	0.5471	1.109	0.1698	0.003
V^E/cm^3·g^{-1}	−0.0067	−0.0004			1.7 10^{-5}
$\Delta\eta$/mPa·s	−345.5	−282.9	−222.3	−284.8	1.85

the molecular mass of the polymer, decreasing as its molecular mass is increased. Since E_{22} is constant for all mixtures, this effect can be related to a decrease of E_{11} and to an increase of E_{12}. Longer polymer chains have two effects: an increase in the relative amount of helical conformations[1,2] and a decrease of the fraction of terminal hydroxyl groups (and of the associated interactions) as compared to the etheric groups in the chain. Both these effects correspond to an increase in E_{12}, since helical (polar) conformations provide additional heteromelecular interactions with the ester O atoms of diethyl carbonate.[19,18] At the same time, E_{11} is reduced by the decrease in the fraction of −OH end groups.

Plots of H^E in Figure 1 show a marked dependence on the molecular mass of the polymer. In contrast, steric effects seem to dominate the trends in Figure 2, since all PEG mixtures display values of V^E less than PPG mixtures, independently of the molecular mass of the polymer.

Curves of $\Delta\eta$ in Figure 3 are mixed together independently of M_w of the polymer. In fact, for each polymer, η increases and $\Delta\eta$ decreases as M_w is increased, but this effect is markedly different for PEG mixtures as compared to PPG mixtures. Plots in Figure 3 show that $\Delta\eta$ is negative for all mixtures. These trends are consistent with an increase in the free volume upon mixing of the components.

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