Densities, Viscosities, and Refractive Indices of New Mixtures of Poly(ethylene glycols) + Dialkyl Carbonates at 313.15 K

Stefano Ottani,*,† Daniele Vitalini,‡ Fabio Comelli,† and Carlo Castellari§

Istituto per la Sintesi Organica e la Fotoreattività (ISOF), C.N.R., c/o Dipartimento di Chimica "G. Ciamician",
Università degli Studi, via Selmi 2, I-40126 Bologna, Italy, Istituto per la Chimica e la Tecnologia dei Polimeri
(ICTP), C.N.R., Viale A. Doria 6, 95125 Catania, Italy, and Dipartimento di Chimica "G. Ciamician",
Alma Mater Studiorum, Università di Bologna, via Selmi 2, I-40126 Bologna, Italy

Densities, viscosities, and refractive indices for binary systems containing mixtures of poly(ethylene glycols) at the same number-average molecular mass ($M_n \approx 300$) but different polydispersities (molecular mass distribution between 1.15 and 1.98) with dimethyl carbonate or diethyl carbonate were determined at 313.15 K and at atmospheric pressure. The measurements were carried out over the whole range of composition, using a vibrating-tube density meter, Ubbelohde viscometers with a Schott-Geräte AVS 310 unit, and an Abbe refractometer. Densities, viscosities, and refractive indices were used to compute the excess volumes, V^E, viscosity deviations, $\Delta\eta$, and deviations in molar refraction, ΔR. Results were fitted to the Redlich−Kister polynomial, and the adjustable parameters were obtained using least-squares methods. The viscosity dependence on temperature was investigated between (309.15 and 327.15) K for some solutions in a restricted composition range. A qualitative discussion on these quantities in terms of molecular interactions is reported.

Introduction

Poly(ethylene glycol) (PEG) is a linear polymer of oxyethylene units with hydroxyl groups at both chain ends. The monomeric unit embodies a hydrophobic region ($-CH_2-CH_2-$) and a H-bonding site ($-O-$), whereas end-groups are strongly hydrophilic. For shorter chains, the hydroxyl end-groups contribute significantly to the physical and chemical properties of PEGs, especially solubility[1] and miscibility in blends,[2] but their importance decreases as chain length is increased. At room temperature, low molecular weight PEGs are viscous fluids or waxy solids, while larger molecular weights correspond to glassy polymers and hard crystalline solids. In the crystal, PEG chains are arranged in 7_2 helical structure (seven monomeric units for two turns of the helix)[3] with an identity period of 2.0 nm.[4] In aqueous solutions, PEG chain conformation seems to depend on the molecular mass: PEG of large molecular mass retains its helical structure, with the hydrophobic methylene groups inside the helix, whereas low molecular mass PEG displays a random coil conformation.[5] Owing to their molecular structure, PEGs are soluble in water and in a large number of organic solvents, a valuable property in processes such as the design of water-soluble catalysts and the purification of biological substances.[6−8] Their solubility, together with their low toxicity and nonirritating nature, has favored the large number of applications of PEGs in the pharmaceutical, petroleum, cosmetic, and food industries.[9−10]

In the present paper, densities, viscosities, and refractive indices have been measured for binary mixtures of PEGs with dimethyl carbonate and diethyl carbonate. These dialkyl carbonates are aprotic solvents with small dipole moments ($\mu = 0.90$ D for diethyl carbonate), typically used in a variety of industrial extraction processes, in the synthesis of pharmaceuticals, and in agricultural chemistry.[11−14]

PEG hydroxyl end-groups can interact via strong H-bonds, developing relatively extended networks of associated molecules. Additional interactions stem from weak H-bonds[15] between methylenes and the O-atoms of the oxymethylene units. Interactions with C=O and $-O-$ groups of dialkyl carbonates can perturb this H-bond network. Previous studies on binary mixtures of PEGs with linear and cyclic ethers showed that excess solution properties depend on the molecular mass of PEG and its molecular mass distribution.[16−18] Possible explanations for this dependence have been based on the changes in the type and strength of homomolecular and heteromolecular H-bonds as the chain length of PEG and its molecular mass distribution are changed.[19]

PEG samples used in this work are mixtures of two polymers with narrow molecular mass distribution. The final samples display similar number-average molar masses but different distributions. Actually, the main purpose of the present work is to investigate effects of molecular mass distribution on the density, viscosity, and refractive index and on the corresponding excess functions of binary mixtures with dialkyl carbonates and to correlate these effects with the type and strength of molecular interactions. Moreover, values of the density, viscosity, and refractive index may show dependencies on the molecular mass and on its distribution that are different from those of the corresponding excess values. For a given set of different PEG grades, it is possible to modify the molecular mass distribution of PEG samples by mixing grades in different proportions. Samples can be prepared with preselected values of the different moments of the molecular mass distribution, such as number- or weight-average molecular

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* To whom correspondence should be addressed. Fax: +39-051-6398349. E-mail: stefano@ciam.unibo.it.

† Istituto per la Sintesi Organica e la Fotoreattività (ISOF), C.N.R.

‡ Istituto per la Chimica e la Tecnologia dei Polimeri (ICTP), C.N.R.

§ Dipartimento di Chimica "G. Ciamician", Alma Mater Studiorum, Università di Bologna.

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Table 1. Properties of Pure Compounds and Comparison with Literature Data at 313.15 K and at Atmospheric Pressure

				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
mix1 (PEG 300 + 400)	296	340	1.15	1.11001		37.395		1.4580	
mix2 (PEG 200 + 400)	295	361	1.22	1.10978		37.749		1.4578	
mix3 (PEG 200 + 600)	290	437	1.51	1.10985		41.664		1.4578	
mix4 (PEG 200 + 1000)	291	577	1.98	1.10972		49.314		1.4578	
dimethyl carbonate				1.04319	1.0418[b]			1.3590	
				1.06334[a]	1.06306[a,c]			1.3666[a]	1.3667[a,d]
					1.0635[a,d]				
diethyl carbonate				0.95243	0.9523[e]			1.3754	
				0.96940[a]	0.96926[a,f]			1.3826[a]	1.3828[a,f]
					0.96940[a,g]				1.3824[a,g]

[a] At 298.15 K. [b] Reference 14. [c] Reference 24. [d] Reference 25. [e] Reference 26. [f] Reference 27. [g] Reference 28.

masses. Thus, the present work may prove useful for the design of PEG samples with a given set of physical properties in solution.

No data have been found in the literature on binary mixtures containing PEGs + dialkyl carbonates.

Experimental Section

Materials. PEGs 200, 300, 400, 600, and 1000 were purchased from Fluka and were used without further purification. These grades were used to prepare four polymeric mixtures, as described later. Dimethyl carbonate and diethyl carbonate were purchased from Aldrich (stated purities > 99%). They were fractionally distilled over sodium in a Vigreux 20-plate column, and the reagent-grade chemicals obtained were further double distilled before use. Purities of the products were checked on a Hewlett-Packard gas chromatograph model 5890 by using an HP (cross-linked 5% ME siloxane) capillary column. Measured purities were >99.8% for both compounds. Before measurements, chemicals were degassed by ultrasound (ultrasonic bath, type 400, Hellma, Milan, Italy), kept in dark bottles, and dried over molecular sieves (Union Carbide, type 4A, 1/16 in. pellets). Solutions of different compositions were prepared by mass in a 25 cm^3 stoppered bottle, using a digital balance (Mettler, model AE 160, Switzerland) accurate to within ±0.0001 g. PEG was weighted first. The second component was injected into the bottle through the stopper by means of a syringe. The whole procedure was similar to the one described in detail elsewhere.[20] All masses were corrected for buoyancy and evaporation of components. Error in the mass fraction was estimated to be less than ±0.0001. In the following, mixtures of two PEG grades will be indicated as polymeric mixtures, whereas we shall refer to binary solutions of these polymeric mixtures with diethyl carbonate or dimethyl carbonate as binary mixtures.

Gel Permeation Chromatography (GPC) Analysis. A PL-GPC 110 (Polymer Laboratories) thermostated system, equipped with three PL-gel 5 μm columns (two mixed-D and one mixed-E) attached in series, was used. The analyses were performed at (35 ± 0.1) °C using THF as the eluant at a flow rate of 1 mL/min. A differential refractometer (Polymer Laboratories) was used as the detector. The instrument was calibrated with a mixture of 7 PEG standards (Polymer Laboratories; molecular masses between 64 and 1450 Da) using the PL-caliber GPC software for the determination of the average molecular masses and polydispersity of the polymer samples.

Sample Preparation. PEG 200, 300, 400, 600, and 1000 were analyzed by GPC, and the number-average, M_n ($=\sum N_iM_i/\sum N_i$), and weight-average, M_w ($=\sum N_iM_i^2/\sum N_iM_i = \sum w_iM_i$), molecular weights were determined. In the above equalities, N_i is the number of moles of species i, having molecular mass M_i and mass fraction w_i. A polydispersity index was obtained as the ratio M_w/M_n. For PEG 200, M_n was equal to 184 and M_w/M_n to 1.108; for PEG 300, M_n = 274 (M_w/M_n = 1.114); for PEG 400, M_n = 365 (M_w/M_n = 1.098); for PEG 600, M_n = 554 (M_w/M_n = 1.060); for PEG 1000, M_n = 923 (M_w/M_n = 1.042).

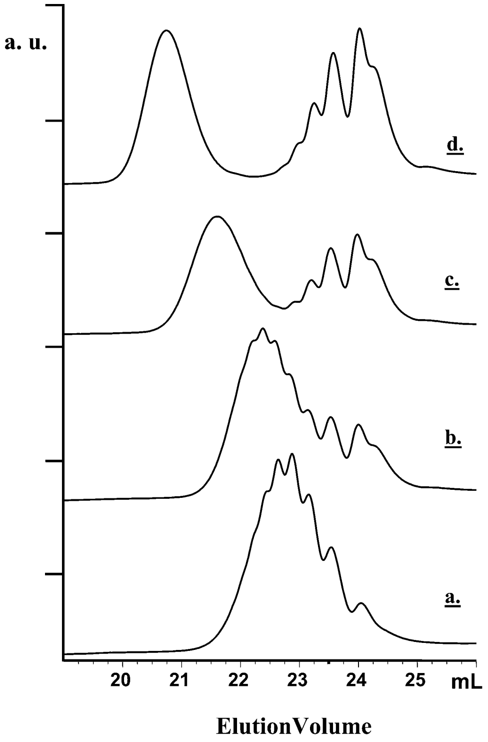

Figure 1. GPC traces of mix1 (a), mix2 (b), mix3 (c), and mix4 (d).

To obtain PEG mixtures of similar M_n (≈300) but different molecular mass distribution, suitable amounts of these grades were mixed and maintained at 50 °C under magnetic stirring for 30 min. The average molecular masses of these polymeric mixtures were subsequently determined by GPC, and the component amounts in each mixture were adjusted to obtain four samples: mix1 (PEG 300, 600 g + PEG 400, 270 g), mix2 (PEG 200, 300 g + PEG 400, 700 g), mix3 (PEG 200, 550 g + PEG 600, 550 g), and mix4 (PEG 200, 550 g + PEG 1000, 500 g). Table 1 reports values of M_n, M_w, and M_w/M_n for these polymeric mixtures, whereas the corresponding GPC traces are reported in Figure 1.

MALDI-TOF Mass Spectrometric Analysis. To ascertain the purity of PEGs used in this work, MALDI-TOF mass spectrometric analysis (by using a Voyager DE-STR instrument from PerSeptive Biosystem) was undertaken using *trans*-3-indoleacrylic acid as a matrix. In the spectra (omitted for brevity), only peaks corresponding to molecules of PEG dihydroxy terminated $H-[O-CH_2-CH_2]_n-OH$ cationized with Na^+ and K^+, together with traces of PEG molecules cationized with H^+, are present. No peaks due to impurities are detected, so the samples can be considered substantially pure.

Density, Kinematic Viscosity, and Refraction Index Measurements. Densities, ρ, of pure components and their binary mixtures were measured by a vibrating-tube density meter (Anton Paar, model DM 60, Graz, Austria) equipped with a measuring cell (Anton Paar, type 602) and a digital thermometer (Anton Paar, DT-40) with precision of ±0.01 K. The apparatus was calibrated periodically with doubly distilled water[21] and dry air.[22] The temperature in the measuring cell was regulated to better than ±0.01 K, using an external bath circulator (Heto, type 01 DBT 623, Birkeròd, Denmark). The uncertainty of density measurements was $\pm 1 \times 10^{-5}$ g·cm^{-3} corresponding to $\pm 3 \times 10^{-3}$ cm^3·mol^{-1} in the excess volumes, $V_m{}^E$. Before measurements, the apparatus was checked by determining V^E_m, the excess molar volume, using the test mixture benzene + cyclohexane at 298.15 K. Our results agree with those of the literature[23] within 1%.

Kinematic viscosities, ν, of pure liquids and mixtures were determined at 313.15 K using several Ubbelohde viscometers with a Schott-Geräte (Mainz, Germany) AVS 310 unit. The viscometers were filled with 15 cm^3 of solution for each measure and immersed in a water bath (Lauda, type E 200, Germany), providing temperature regulation with an accuracy of ±0.01 K. Several viscometers were used, with capillary diameters from (0.36 to 1.13) mm, for kinematic ranges of (0.6 to 40) mm^2·s^{-1}, respectively. The kinematic viscosities were determined according to the equation

$$\nu = \eta/\rho = k(t - \theta) \tag{1}$$

where η is the absolute (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. The calibration of the viscometers was carried out with double distilled water and by a standard oil specimen of known viscosity. Quintuplicate measurements of flow times were reproducible within ±0.06%. The uncertainty of the viscosity measurements was ±0.5%. In the whole set of experiments, flow times were maintained at >200 s, by selecting viscometers with appropriate values of k.

Viscosities of polymeric and of some binary mixtures were also measured at (309.15, 311.15, 315.15, 319.15, 323.15, and 327.15) K by a shear-controlled rotary rheometer (Rotovisco RV20 by Haake Mess-Technik GmbH), driven by a computer through a Rheocontroller RC20B apparatus. The M5 Searle-type measuring system and the NV sensor were used. Both the cup and the vessel were thermostated by a Haake F3 circulator, connected through thermally insulated hoses. Temperature control was within ±0.05 K. The apparatus was calibrated by standard specimens of known viscosity, provided by Haake. The experimental assembly allows measurement of viscosities in the range (20 to 9×10^3) mPa·s with an uncertainty of ±1.5%. Details of the experimental apparatus and procedure have been reported.[16] Preliminary tests showed that the investigated specimens display Newtonian behavior at shear rates ranging from (0 to 900) s^{-1}. For each mixture, 9 cm^3 was introduced in the cup at 309.15 K and viscosity was obtained as the average of 30 measurements at constant shear rate. Then, the temperature was increased and allowed to stabilize and the procedure was repeated to obtain another value of the viscosity. Different constant shear rates were selected in the range (200 to 800) s^{-1}, depending on the temperature and on the mixture composition. The rotary rheometer was preferred over the Ubbelohde viscometers, because the overall time to perform experiments is considerably shorter, avoiding biases related to evaporation of the highly volatile component.

The refractive indices at the sodium line, n_D, were measured by a thermostated Abbe refractometer (Carl Zeiss, model G, Jena, Switzerland). Uncertainty on the refractive index values was <0.0001 units. An average of five measurements was taken for each sample.

Densities, viscosities, and refractive indices of pure compounds are reported in Table 1 together with the corresponding literature values.[14,24−28]

Results and Discussion

The experimental values of density, viscosity, and refractive indices for binary mixtures at 313.15 K and at atmospheric pressure are reported in Tables 2 and 3 versus the PEG mass fraction. Excess volumes, V^E, are calculated on a mass basis (cm^3·g^{-1}) according to the following equation:

$$V^E = 1/\rho - w_1/\rho_1 - w_2/\rho_2 \tag{2}$$

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. PEGs investigated in this work are polymeric mixtures of larger polydispersity, as compared to the molecular mass distributions of the constituents.[16] Thus, mass fractions have been preferred, to avoid problems related to the evaluation of molar fractions for these compounds. Values of V^E are reported in Table 2 and Figure 2 and are negative for all mixtures. V^E values of mixtures with diethyl carbonate are constantly more negative than the corresponding values of mixtures with dimethyl carbonate.

Deviations in viscosity, $\Delta\eta$, are defined by the relation

$$\Delta\eta = \eta - (w_1\eta_1 + w_2\eta_2) \tag{3}$$

where η, η_1, and η_2 are the dynamic viscosities of the binary mixture and pure components 1 and 2, respectively. Values of $\Delta\eta$ are reported in Table 2 and Figure 3 and are negative for all mixtures. In contrast to the trends reported in Figure 2, diethyl carbonate and dimethyl carbonate solutions are not separated in two distinct groups. In fact, for these mixtures, values of $\Delta\eta$ decrease systematically as the molecular weight of the PEG mixture is increased, with dimethyl carbonate solution always below the corresponding diethyl carbonate curve. Minima are located at $w_1 \approx 0.7$.

The molar refraction deviation, ΔR, was calculated from the Lorentz−Lorenz[29,30] equation

$$\Delta R = R_m - \sum_{i=1}^{2} R_i\varphi_i \tag{4}$$

where R_i and R_m are the molar refractions of pure components and of the mixture, respectively, and φ_i is the volume fraction of the ith component, given as

$$\varphi_i = x_iV_i \Big/ \sum_{i=1}^{2} x_iV_i \tag{5}$$

where $V_i = M_i/\rho_i$.

Table 2. Densities, ρ, Excess Volumes, V^E, and Viscosity Deviations, $\Delta\eta$, for PEG Mixtures + Dimethyl Carbonate or + Diethyl Carbonate at 313.15 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)
Mix1 (PEG 300 + 400) (1) + Dimethyl Carbonate (2)									
0.0515	1.04712	−0.0005	0.572	−1.819	0.6276	1.08754	−0.0028	5.303	−18.350
0.0899	1.04987	−0.0007	0.670	−3.137	0.7204	1.09349	−0.0024	8.170	−18.908
0.2119	1.05873	−0.0017	1.010	−7.300	0.7969	1.09819	−0.0019	12.225	−17.676
0.3032	1.06531	−0.0023	1.484	−10.197	0.8800	1.10321	−0.0013	18.903	−14.066
0.4323	1.07436	−0.0027	2.257	−14.187	0.9149	1.10524	−0.0010	22.849	−11.405
0.5066	1.07949	−0.0029	3.057	−16.131	0.9579	1.10769	−0.0005	29.425	−6.416
Mix1 (PEG 300 + 400) (1) + Diethyl Carbonate (2)									
0.0568	0.96060	−0.0005	0.724	−1.994	0.6538	1.05332	−0.0032	6.683	−17.983
0.1080	0.96813	−0.0010	0.837	−3.763	0.7315	1.06590	−0.0028	9.514	−18.006
0.2349	0.98719	−0.0020	1.271	−7.994	0.8013	1.07727	−0.0023	13.300	−16.785
0.3164	0.99962	−0.0025	1.701	−10.562	0.8848	1.09096	−0.0015	20.214	−12.940
0.4534	1.02110	−0.0031	2.880	−14.418	0.9234	1.09728	−0.0010	24.781	−9.794
0.5280	1.03298	−0.0032	3.903	−16.137	0.9602	1.10334	−0.0006	30.173	−5.755
Mix2 (PEG 200 + 400) (1) + Dimethyl Carbonate (2)									
0.0370	1.04590	−0.0004	0.544	−1.324	0.6295	1.08739	−0.0028	5.365	−18.580
0.0878	1.04961	−0.0008	0.634	−3.127	0.7180	1.09304	−0.0024	8.070	−19.172
0.2062	1.05817	−0.0017	0.947	−7.225	0.7890	1.09745	−0.0020	11.602	−18.286
0.2998	1.06484	−0.0022	1.330	−10.332	0.8747	1.10245	−0.0012	18.438	−14.642
0.4243	1.07358	−0.0027	2.221	−14.077	0.9199	1.10517	−0.0009	23.767	−10.998
0.5079	1.07932	−0.0029	3.217	−16.197	0.9728	1.10822	−0.0003	32.328	−4.409
Mix2 (PEG 200 + 400) (1) + Diethyl Carbonate (2)									
0.0453	0.95888	−0.0003	0.701	−1.612	0.6546	1.05313	−0.0029	6.787	−18.144
0.0932	0.96589	−0.0008	0.804	−3.286	0.7382	1.06679	−0.0027	9.922	−18.110
0.2237	0.98549	−0.0019	1.268	−7.668	0.7992	1.07690	−0.0024	13.291	−17.005
0.3186	1.00000	−0.0025	1.773	−10.683	0.8806	1.09039	−0.0017	20.457	−12.862
0.4511	1.02073	−0.0031	2.902	−14.474	0.9590	1.10323	−0.0007	30.185	−6.044
0.5268	1.03266	−0.0031	3.929	−16.257	0.9850	1.10741	−0.0003	34.732	−2.461
Mix3 (PEG 200 + 600) (1) + Dimethyl Carbonate (2)									
0.0498	1.04690	−0.0005	0.618	−1.923	0.6311	1.08745	−0.0027	5.871	−20.604
0.0863	1.04947	−0.0007	0.640	−3.402	0.7172	1.09302	−0.0024	8.858	−21.163
0.2060	1.05810	−0.0016	0.978	−7.993	0.7823	1.09704	−0.0020	12.383	−20.319
0.2951	1.06447	−0.0021	1.370	−11.272	0.8804	1.10301	−0.0013	20.971	−15.770
0.4236	1.07351	−0.0027	2.315	−15.617	0.9093	1.10468	−0.0010	24.726	−13.205
0.5070	1.07922	−0.0028	3.323	−18.042	0.9585	1.10750	−0.0005	32.728	−7.227
Mix3 (PEG 200 + 600) (1) + Diethyl Carbonate (2)									
0.0628	0.96139	−0.0005	0.766	−2.443	0.6480	1.05216	−0.0031	7.128	−20.092
0.0933	0.96586	−0.0008	0.817	−3.642	0.7193	1.06402	−0.0030	9.893	−20.254
0.2249	0.98559	−0.0019	1.277	−8.584	0.8008	1.07783	−0.0029	14.653	−18.837
0.3650	1.00711	−0.0027	2.194	−13.414	0.8789	1.09096	−0.0025	21.702	−14.991
0.4541	1.02094	−0.0029	3.151	−16.113	0.9139	1.09663	−0.0020	26.183	−11.946
0.5202	1.03141	−0.0030	4.088	−17.887	0.9548	1.10309	−0.0012	32.615	−7.194
Mix4 (PEG 200 + 1000) (1) + Dimethyl Carbonate (2)									
0.0443	1.04646	−0.0004	0.613	−2.043	0.6397	1.08783	−0.0025	6.987	−24.736
0.0973	1.05029	−0.0008	0.720	−4.522	0.7224	1.09315	−0.0023	10.560	−25.199
0.2342	1.06014	−0.0018	1.079	−10.847	0.8061	1.09839	−0.0018	16.370	−23.479
0.2935	1.06434	−0.0021	1.479	−13.341	0.8764	1.10263	−0.0013	24.144	−19.138
0.4360	1.07421	−0.0026	2.790	−18.986	0.9262	1.10553	−0.0008	32.183	−13.527
0.5148	1.07956	−0.0027	3.910	−21.713	0.9633	1.10764	−0.0004	39.900	−7.620
Mix4 (PEG 200 + 1000) (1) + Diethyl Carbonate (2)									
0.0687	0.96235	−0.0006	0.776	−3.201	0.6606	1.05414	−0.0030	8.653	−24.135
0.1531	0.97479	−0.0013	1.041	−7.043	0.7436	1.06758	−0.0026	12.866	−23.964
0.2307	0.98647	−0.0019	1.421	−10.440	0.8164	1.07952	−0.0021	18.464	−21.913
0.3214	1.00041	−0.0025	1.987	−14.290	0.8877	1.09118	−0.0014	26.681	−17.163
0.4591	1.02198	−0.0031	3.586	−19.396	0.9282	1.09785	−0.0010	33.283	−12.536
0.5337	1.03374	−0.0032	4.909	−21.703	0.9624	1.10344	−0.0005	40.043	−7.437

The molar refraction, R_i, was obtained from the formula (Lorentz−Lorenz)

$$R_i = \{[n^2_{D(i)} - 1]/[n^2_{D(i)} + 2]\}V_i \qquad (6)$$

where $n_{D(i)}$ is the refractive index for the pure ith component.

The equation for binary mixtures becomes

$$R_m = \{[n^2_{D(m)} - 1]/[n^2_{D(m)} + 2]\}V_m \qquad (7)$$

where $n_{D(m)}$ is the refractive index of the mixture, $V_m = (x_1M_1 + x_2M_2)/\rho$, and x_1 and x_2 are the molar fractions of components 1 and 2, respectively. Accuracy in the calculation of R_m and ΔR was ±0.0001 cm^3·mol^{-1}. Deviations in refractive indices are reported in Table 3 and Figure 4. They are all negative, with all dimethyl carbonate solutions below mixtures with diethyl carbonate.

Changes in V^E, $\Delta\eta$, and ΔR with composition can be expressed by the Redlich−Kister equation[31]

$$Q^E_{calc} = w_1w_2\sum_{k\geq 0}a_k(w_1 - w_2)^k \qquad (8)$$

where Q^E_{calc} refers to V^E, $\Delta\eta$, or ΔR. The adjustable parameters a_k were determined by a least-squares method,

Table 3. Refractive Indices, n_D, and Deviations in Refractive Indices, ΔR, for PEG Mixtures + Dimethyl Carbonate or + Diethyl Carbonate at 313.15 K

w_1	n_D	ΔR/(cm^3·mol^{-1})	w_1	n_D	ΔR/(cm^3·mol^{-1})
Mix1 (PEG 300 + 400) (1) + Dimethyl Carbonate (2)					
0.0515	1.3643	−1.714	0.6276	1.4218	−14.612
0.0899	1.3680	−2.970	0.7204	1.4312	−14.285
0.2119	1.3803	−6.717	0.7969	1.4388	−12.894
0.3032	1.3993	−8.671	0.8800	1.4469	−9.701
0.4323	1.4023	−12.214	0.9149	1.4505	−7.611
0.5066	1.4096	−13.506	0.9579	1.4544	−4.297
Mix1 (PEG 300 + 400) (1) + Diethyl Carbonate (2)					
0.0568	1.3798	−1.121	0.6538	1.4286	−8.254
0.1080	1.3835	−2.119	0.7315	1.4355	−7.820
0.2349	1.3938	−4.351	0.8013	1.4414	−6.923
0.3164	1.4003	−5.626	0.8848	1.4486	−4.948
0.4534	1.4116	−7.322	0.9234	1.4520	−3.600
0.5280	1.4179	−7.931	0.9602	1.4551	−2.027
Mix2 (PEG 200 + 400) (1) + Dimethyl Carbonate (2)					
0.0370	1.3635	−1.194	0.6295	1.4218	−14.513
0.0878	1.3682	−2.865	0.7180	1.4307	−14.207
0.2062	1.3805	−6.466	0.7890	1.4378	−12.997
0.2998	1.3890	−9.092	0.8747	1.4462	−9.881
0.4243	1.4017	−11.952	0.9199	1.4507	−7.210
0.5079	1.4098	−13.416	0.9728	1.4558	−2.839
Mix2 (PEG 200 + 400) (1) + Diethyl Carbonate (2)					
0.0453	1.3787	−0.902	0.6546	1.4284	−8.195
0.0932	1.3825	−1.813	0.7382	1.4356	−7.731
0.2237	1.3928	−4.141	0.7992	1.4407	−6.957
0.3186	1.4003	−5.628	0.8806	1.4484	−5.022
0.4511	1.4113	−7.250	0.9590	1.4546	−2.135
0.5268	1.4175	−7.880	0.9850	1.4569	−0.819
Mix3 (PEG 200 + 600) (1) + Dimethyl Carbonate (2)					
0.0498	1.3640	−1.602	0.6311	1.4218	−13.987
0.0863	1.3675	−2.752	0.7172	1.4300	−13.717
0.2060	1.3794	−6.303	0.7823	1.4367	−12.666
0.2951	1.3882	−8.689	0.8804	1.4463	−9.234
0.4236	1.4009	−11.572	0.9093	1.4492	−7.619
0.5070	1.4092	−12.960	0.9585	1.4539	−4.054
Mix3 (PEG 200 + 600) (1) + Diethyl Carbonate (2)					
0.0628	1.3807	−1.140	0.6480	1.4278	−7.787
0.0933	1.3824	−1.740	0.7193	1.4339	−7.492
0.2249	1.3927	−3.982	0.8008	1.4410	−6.557
0.3650	1.4039	−5.980	0.8789	1.4475	−4.902
0.4541	1.4114	−6.928	0.9139	1.4507	−3.794
0.5202	1.4168	−7.452	0.9548	1.4542	−2.206
Mix4 (PEG 200 + 1000) (1) + Dimethyl Carbonate (2)					
0.0443	1.3635	−1.435	0.6397	1.4225	−14.121
0.0973	1.3688	−3.105	0.7224	1.4307	−13.757
0.2342	1.3820	−7.148	0.8061	1.4391	−12.169
0.2935	1.3880	−8.711	0.8764	1.4458	−9.526
0.4360	1.4021	−11.892	0.9262	1.4507	−6.601
0.5148	1.4099	−13.166	0.9633	1.4542	−3.696
Mix4 (PEG 200 + 1000) (1) + Diethyl Carbonate (2)					
0.0687	1.3806	−1.301	0.6606	1.4287	−7.865
0.1531	1.3871	−2.818	0.7436	1.4357	−7.380
0.2307	1.3931	−4.117	0.8164	1.4421	−6.347
0.3214	1.4003	−5.474	0.8877	1.4480	−4.675
0.4591	1.4117	−7.067	0.9282	1.4516	−3.304
0.5337	1.4178	−7.633	0.9624	1.4546	−1.884

by fitting the experimental values to eq 8. The corresponding results are reported in Table 4. The tabulated standard deviations, $\sigma(Q^E)$, reported in Table 4, are defined as

$$\sigma(Q^E) = |\phi_{\min}/(N - n)|^{0.5} \qquad (9)$$

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

$$\phi = \sum_{k=1}^{N} (Q^E_{\text{calc}} - Q^E)^2 \qquad (10)$$

where Q^E is the experimental value. The full lines in Figures 2−4 correspond to the Redlich−Kister polynomials.

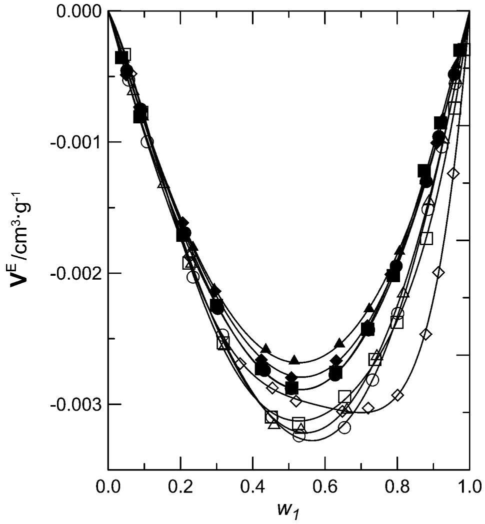

Figure 2. Excess volumes, V^E, vs the mass fraction, w_1, of PEG mixtures + dimethyl carbonate (full points) or + diethyl carbonate (open points) at 313.15 K. (●, ○), (■, □), (◆, ◇), and (▲, △) refer to mix1, mix2, mix3, and mix4, respectively. Full lines correspond to the Redlich−Kister polynomial.

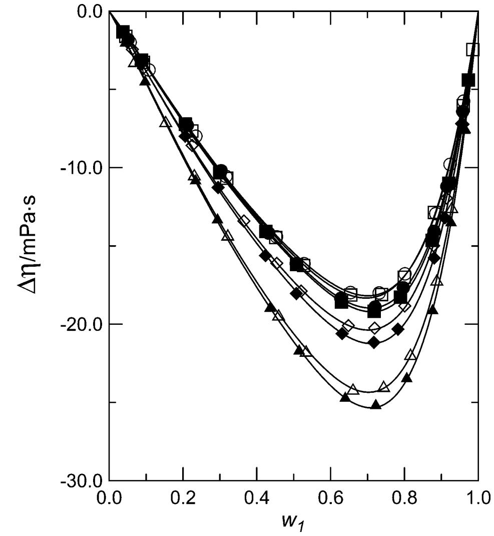

Figure 3. Viscosity deviations, $\Delta\eta$, vs the mass fraction, w_1, of PEG mixtures + dimethyl carbonate (full points) or + diethyl carbonate (open points) at 313.15 K. (●, ○), (■, □), (◆, ◇), and (▲, △) refer to mix1, mix2, mix3, and mix4, respectively. Full lines correspond to the Redlich−Kister polynomial.

When possible, the viscosity of binary solutions was also measured by the rotary rheometer. Table 5 reports values of η at different temperatures for these solutions. Values of η versus T have been correlated by an Arrhenius type equation:

$$\eta = A \exp\left(\frac{E_{\text{att}}}{RT}\right) \qquad (11)$$

where A and E_{att} are adjustable parameters and R is the ideal gas constant. Since all the investigated mixtures display Newtonian behavior, E_{att} can be interpreted, according to Eyring's model for viscous flow,[32] as the activation energy related to molecular jumps under the effect of the applied shear stress. Values in Table 5 show that E_{att} decreases as the polymer mass fraction is decreased.

Data in Table 1 show that values of ρ and n_D of polymer mixtures are almost identical, independently of M_w and molecular mass distribution. Moreover, as reported in

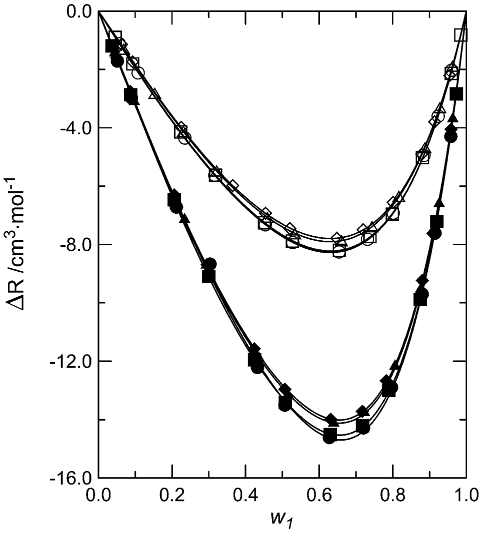

Figure 4. Deviations in refractive indices, ΔR, vs the mass fraction, w_1, of PEG mixtures + dimethyl carbonate (full points) or + diethyl carbonate (open points) at 313.15 K. (●, ○), (■, □), (◆, ◇), and (▲, △) refer to mix1, mix2, mix3, and mix4, respectively. Full lines correspond to the Redlich−Kister polynomial.

Table 4. Adjustable Parameters, a_k, from Equation 8, and Standard Deviations $\sigma(Q_m^E)$, Equation 9, of PEG Mixtures + Dialkyl Carbonates at 313.15 K

function	a_0	a_1	a_2	a_3	$\sigma(Q_m^E)$
Mix1 (PEG 300 + 400) (1) + Dimethyl Carbonate (2)					
$V^E/cm^3 \cdot g^{-1}$	−0.0115	−0.0017	−0.0010	−0.0001	1.5×10^{-5}
$\Delta\eta$/mPa·s	−63.3480	−48.2845	−38.7612	−22.3973	0.126
$\Delta R/cm^3 \cdot mol^{-1}$	−53.029	−32.170	−18.961	−6.9771	0.164
Mix1 (PEG 300 + 400) (1) + Diethyl Carbonate (2)					
$V^E/cm^3 \cdot g^{-1}$	−0.0129	−0.0037	0.0004	0.0015	2.6×10^{-5}
$\Delta\eta$/mPa·s	−61.7726	−44.6017	−35.3834	−20.7058	0.079
$\Delta R/cm^3 \cdot mol^{-1}$	−30.901	−15.563	−7.2262	−2.6472	0.012
Mix2 (PEG 200 + 400) (1) + Dimethyl Carbonate (2)					
$V^E/cm^3 \cdot g^{-1}$	−0.0115	−0.0019	0.0010	0.0016	2.5×10^{-5}
$\Delta\eta$/mPa·s	−63.8645	−48.5744	−41.1177	−24.0797	0.065
$\Delta R/cm^3 \cdot mol^{-1}$	−53.023	−29.694	−18.413	−10.550	0.039
Mix2 (PEG 200 + 400) (1) + Diethyl Carbonate (2)					
$V^E/cm^3 \cdot g^{-1}$	−0.0125	−0.0012	−0.0008	−0.0057	2.5×10^{-5}
$\Delta\eta$/mPa·s	−62.4311	−45.8466	−33.8429	−17.1553	0.138
$\Delta R/cm^3 \cdot mol^{-1}$	−30.711	−15.461	−7.3557	−2.9397	0.018
Mix3 (PEG 200 + 600) (1) + Dimethyl Carbonate (2)					
$V^E/cm^3 \cdot g^{-1}$	−0.0111	−0.0018	0.0004	0.0002	2.4×10^{-5}
$\Delta\eta$/mPa·s	−70.9170	−53.1330	−44.5864	−27.7418	0.114
$\Delta R/cm^3 \cdot mol^{-1}$	−51.230	−28.207	−18.032	−10.297	0.046
Mix3 (PEG 200 + 600) (1) + Diethyl Carbonate (2)					
$V^E/cm^3 \cdot g^{-1}$	−0.0118	−0.0021	−0.0077	−0.1176	2.4×10^{-5}
$\Delta\eta$/mPa·s	−69.1214	−49.9681	−40.0260	−23.4630	0.091
$\Delta R/cm^3 \cdot mol^{-1}$	−29.199	−14.170	−7.2314	−4.0724	0.015
Mix4 (PEG 200 + 1000) (1) + Dimethyl Carbonate (2)					
$V^E/cm^3 \cdot g^{-1}$	−0.0107	−0.0011	−0.0002	−0.0008	1.8×10^{-5}
$\Delta\eta$/mPa·s	−84.4986	−64.1224	−52.9176	−31.1835	0.092
$\Delta R/cm^3 \cdot mol^{-1}$	−51.619	−28.346	−18.237	−10.889	0.052
Mix4 (PEG 200 + 1000) (1) + Diethyl Carbonate (2)					
$V^E/cm^3 \cdot mol^{-1}$	−0.0128	−0.0026	0.0012	−0.0008	2.3×10^{-5}
$\Delta\eta$/mPa·s	−82.4474	−59.8865	−47.8995	−29.2637	0.121
$\Delta R/cm^3 \cdot mol^{-1}$	−29.584	−14.520	−7.0725	−3.5343	0.014

Table 5. Viscosities, η, at Different Temperatures and Compositions of PEG Mixtures + Dialkyl Carbonates, Measured by the Rotovisco RV20[a]

	η/(mPa·s) at the following T/K						E_{att}
w_1	309.15	311.15	315.15	319.15	323.15	327.15	kJ·mol⁻¹
Mix1 (PEG 300 + 400) (1) + Dimethyl Carbonate (2)							
0.7969	22.90	21.24	18.49	16.33	14.67	13.42	16.9
0.8800	14.97	14.29	12.60	11.16	10.82	10.34	24.5
0.9149	27.37	25.29	21.86	18.88	16.61	14.80	28.6
0.9579	35.76	32.83	28.09	24.06	20.78	18.24	31.2
1.0000	46.56	42.71	36.26	30.94	26.14	22.82	32.9
Mix1 (PEG 300 + 400) (1) + Diethyl Carbonate (2)							
0.7315	11.95	11.29	10.17	9.51	8.74	8.19	16.0
0.8013	16.41	15.39	13.55	12.23	11.25	10.38	20.4
0.8848	24.92	22.94	19.95	17.37	15.58	14.45	25.2
0.9234	30.89	28.16	24.34	21.03	18.39	16.02	29.6
0.9602	37.20	34.00	28.80	25.07	21.74	19.01	30.7
Mix2 (PEG 200 + 400) (1) + Dimethyl Carbonate (2)							
0.7180	9.73	9.12	8.27	7.52	7.08	6.82	15.9
0.7890	14.26	13.54	11.57	10.75	9.95	9.29	19.2
0.8747	22.37	20.58	18.38	16.02	14.09	12.67	25.9
0.9199	29.48	26.73	23.34	20.08	17.83	15.57	28.7
0.9728	40.16	37.07	31.70	26.14	22.85	20.07	32.4
1.0000	47.22	43.23	36.77	31.38	26.36	23.22	32.9
Mix2 (PEG 200 + 400) (1) + Diethyl Carbonate (2)							
0.7382	12.09	11.42	10.71	10.07	9.42	8.68	13.4
0.7992	16.04	15.39	13.53	12.04	11.65	10.79	17.9
0.8806	24.87	23.28	19.88	17.48	15.26	13.81	27.4
0.9590	36.39	33.89	28.55	24.62	21.65	18.65	30.9
0.9850	42.88	39.45	33.29	27.92	24.51	21.10	32.7
Mix3 (PEG 200 + 600) (1) + Dimethyl Carbonate (2)							
0.7823	15.47	14.73	13.68	12.82	12.07	11.38	12.4
0.8804	25.70	24.10	21.13	19.03	17.59	16.04	21.0
0.9093	29.72	27.78	23.90	21.04	18.48	16.52	27.2
0.9585	40.52	37.26	31.76	27.34	23.83	21.05	30.1
1.0000	52.13	47.71	40.62	34.58	29.98	26.04	31.7
Mix3 (PEG 200 + 600) (1) + Diethyl Carbonate (2)							
0.7193	12.27	11.73	10.54	9.76	9.17	8.63	15.1
0.8008	18.22	16.94	15.24	14.87	13.79	12.53	14.7
0.8789	27.41	25.24	22.22	19.35	17.29	15.63	25.2
0.9139	32.77	30.36	26.05	22.56	19.74	17.65	28.4
0.9548	40.84	36.91	31.52	27.64	23.82	20.82	30.3
Mix4 (PEG 200+1000) (1) + Dimethyl Carbonate (2)							
0.8061	18.81	17.95	15.77	14.15	12.79	12.15	21.1
0.8764	29.59	27.26	23.67	20.71	18.26	16.29	27.2
0.9262	39.16	35.89	30.71	26.55	23.21	20.44	29.9
0.9633	46.77	43.47	37.04	31.71	27.30	23.97	31.6
1.0000	61.61	56.51	48.01	41.11	35.44	30.78	31.7
0.8061	18.81	17.95	15.77	14.15	12.79	12.15	21.1
Mix4 (PEG 200 + 1000) (1) + Diethyl Carbonate (2)							
0.7436	15.22	14.33	12.92	11.90	11.17	10.47	16.6
0.8164	21.51	20.08	17.78	15.74	13.99	12.99	23.7
0.8877	31.57	29.34	25.43	22.08	19.46	17.45	27.7
0.9282	39.06	36.20	30.90	26.58	23.13	20.49	30.4
0.9624	48.45	44.63	37.87	32.43	28.04	24.55	31.6

[a] Activation energies for viscous flow, E_{att}, computed by eq 11.

Tables 2 and 3, values of ρ and n_D, for the same dialkyl carbonate solution at the same mass fraction, are quite similar and almost independent of the polymer component. Density values for diethyl carbonate mixtures are always less than the corresponding values of dimethyl carbonate mixtures. In contrast, n_D values of binary solutions with diethyl carbonate are larger in the whole composition range. Similar trends are obtained with the corresponding values of V^E and ΔR. As reported in Figures 2 and 4, plots of V^E and ΔR versus w_1 can be separated in two groups, depending on the type of dialkyl carbonate. V^E curves for dimethyl carbonate mixtures are always above the corresponding diethyl carbonate curves, whereas for ΔR the trends are opposite. In contrast, η and $\Delta\eta$ behave somehow differently. Table 2 and Figure 3 show that plots of $\Delta\eta$ for diethyl carbonate solutions are always above the corresponding dimethyl carbonate solutions only for PEG mix1 and mix2.

Conclusions

Data on binary mixtures can be interpreted by considering two fundamental features of these systems: the differences in the solvent effect, stemming from the different steric hindrance and flexibility of the $-CH_3$ and $-C_2H_5$

groups of dimethyl carbonate and diethyl carbonate, respectively, and the effect of the different chain length distributions in PEG specimens. Actually, values of M_w in Table 1 show that the mass fraction of longer chains increases from mix1 to mix4, whereas the average number of repeating units per chain molecule remains constant ($M_n \approx 300$). Values of V^E and ΔR, reported in Figures 2 and 4, display significant changes as dimethyl carbonate is replaced by diethyl carbonate, whereas the influence of longer chain tails on going from mix1 to mix4 seems negligible. Thus, the lower values of V^E for the diethyl carbonate solutions can be explained by closer molecular packing between polymer and diethyl carbonate molecules, stemming from the increased flexibility of the $-C_2H_5$ group as compared to the $-CH_3$ group of dimethyl carbonate. In contrast, as reported in Figure 3, values of $\Delta\eta$ for PEG mix3 and mix4 are below the curves of mix1 and mix2 solutions, independently of the solvent. These trends suggest that the effect of M_w (corresponding to larger fractions of longer chains) on $\Delta\eta$ is more important than changes in the flexibility of solvent molecules.

Data in Tables 1 and 5 show that η increases as M_w is increased. For polymers below M_{cr}, the critical molecular mass for development of entanglement, the correlation between η and M_w can be described by the equation $\ln \eta = C_1 + C_2(M_w)^{1/2}$, where C_1 and C_2 are empirical constants.[33] For PEG, the value of M_{cr} is 3400 Da.[33] Application of this equation to the viscosities of PEGs reported in Table 5 leads to values of C_2 between 0.051 and 0.055 in the investigated temperature range.

Data reported in Tables 1 and 5 and Figures 2 and 3 lead to the conclusion that for $M_n \approx 300$, changes in the polydispersity have scarce or no influence upon densities and excess volumes. In contrast, such changes significantly affect the viscosities of polymer mixtures and solutions.

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