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Densities, Viscosities, and Refractive Indices of Poly(ethylene glycol) 200 and 400 + Cyclic Ethers at 303.15 K

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Densities, ρ, kinematic viscosities, ν, and refractive indices, n_D, were determined for poly(ethylene glycol) 200 and 400 + 1,3-dioxolane, + 1,4-dioxane, + oxolane (tetrahydrofuran, THF), and + oxane (tetrahydropyran, THP) binary mixtures over the entire range of composition at 303.15 K and at atmospheric pressure. The excess molar volumes, V_m^E, deviations in viscosities, $\Delta\eta$, and deviations in molar refractions, ΔR, calculated from experimental measurements, are always negative. The results were correlated with the Redlich−Kister polynomial. The McAllister multibody interaction model was used to correlate the kinematic viscosities of liquid mixtures with mole fractions. The viscosity dependence on temperature was investigated between 297.15 and 309.15 K for some solutions in a restricted composition range.

Introduction

The thermodynamic and transport properties of polymers are especially relevant in polymer processing and industrial applications. Correlations between molecular weight and physical properties of polymers have been largely investigated, mostly in the high molecular weight range ($>10^4$ Da), while studies on low molecular weight polymers are less frequent. Nonetheless, several industrial applications make use of such substances, such as poly(ethylene glycol) (PEG), poly(propylene glycol), and their copolymers. Because of their low toxicity, PEGs are frequently used in the pharmaceutical and cosmetic fields as solvents, carriers, humectants, lubricants, binders, bases, and coupling agents[1] and also for extraction, separation, and purification of biological materials.[2,3]

PEGs are linear polymeric materials whose chains are composed by oxyethylene units and terminated by hydroxyl groups at both ends. Depending on their average molecular weight, they can be liquids (200−800 Da), waxy solids (1000−1500 Da), and flakes or solids (2000−10000 Da). Since end-group effects are considered less important as the molecular weight is increased, PEGs of higher average molecular weight (>10000 Da) are commercialized as poly(ethylene oxide). The presence of reactive terminal groups makes these materials suitable for the synthesis of polyesters and polyurethanes.[4]

Although some works have been made on the characterization of water solutions of different average molecular weight PEGs, few data are reported in the literature on mixtures of PEGs with organic solvents. In the present work, solutions of PEG 200 and 400 in four cyclic ethers, namely, 1,3-dioxolane, 1,4-dioxane, oxolane (THF), and oxane (THP) were investigated. Such ethers contain one or two oxygen atoms that can interact via H-bonds with the hydroxyl groups of the polymer. Measurements of the densities, ρ, kinematic viscosities, ν, and refractive indices, n_D, were performed at 303.15 K under atmospheric pressure and the results were fitted to the Redlich−Kister polynomial. The McAllister multibody model was used to correlate the kinematic viscosities. In addition, viscosities of PEG 200, PEG 400 + oxolane, and oxane were measured at different temperatures in the interval (297.15 to 309.15) K for polymer molar fractions ranging from 0.5 to 1.0. The aim of this work is to obtain information about these mixtures, to investigate correlations among them, and to provide a qualitative interpretation in terms of molecular interactions. No data have been previously reported in the literature on these mixtures.

Materials and Methods

Materials. PEG 200 and 400 (Fluka product) were used without further purification. Their number average molecular weights (M_n), determined by gel permeation chromatography (GPC), were 192 and 408, respectively. 1,3-Dioxolane (Aldrich >99.8%), 1,4-dioxane (Fluka >99.8%), oxane (Aldrich >99%), and oxolane (Aldrich >99.9%) were used without further purification. Cyclic ethers were degassed by ultrasound (ultrasonic bath, Hellma, type 460, Milan, Italy). All chemicals were kept in dark bottles and dried over molecular sieves (Union Carbide, type 4A, 1/16 in. pellets).

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 seven PEG standards (Polymer Laboratories; molecular masses between 64 Da and 1450 Da) using the PL-caliber GPC software for the determination of the average molecular masses and polydispersity of the polymer samples.

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

		ρ (g·cm^{-3})		η (mPa·s)		n_D	
compound	T (K)	this work	lit.	this work	lit.	this work	lit.
PEG 200	298.15	1.12098		48.157		1.4585	
	303.15	1.11701		37.682		1.4570	
PEG 400	298.15	1.12249	1.12230[7]	92.797		1.4650	
	303.15	1.11831		71.776		1.4638	
1,3-dioxolane	293.15	1.06477	1.0647[8]			1.3994	1.3992[8]
	298.15	1.05886	1.05865[9]	0.592		1.3983	1.3984[10]
	303.15	1.05268		0.558		1.3962	
1,4-dioxane	298.15	1.02806	1.02797[9]	1.202	1.196[11] 1.262[12]	1.4201	1.42025[8]
	303.15	1.02244	1.022219[13]	1.100	1.096[14]	1.4177	1.418[15]
oxolane	298.15	0.88190	0.88193[16]	0.468	0.460[8]	1.4048	1.40496[8]
	303.15	0.87636		0.442		1.4025	1.4026[17]
oxane	298.15	0.87931	0.8791[9] 0.8742[18]	0.813		1.4188	1.41862[8] 1.4159[18]
	303.15	0.87431		0.758		1.4165	

Table 2. Densities, ρ, and Dynamic Viscosities, η, at Different Temperatures of PEG 200, PEG 400, Oxolane, and Oxane

	PEG200		PEG400		oxolane		oxane	
T (K)	ρ (g·cm^{-3})	η (mPa·s)	ρ (g·cm^{-3})	η (mPa·s)	ρ (g·cm^{-3})	η (mPa·s)	ρ (g·cm^{-3})	η (mPa·s)
297.15	1.12231	50.686	1.12381	97.909	0.88261	0.473	0.87991	0.824
298.15	1.12098	48.157	1.12249	92.797	0.88186	0.468	0.87931	0.813
299.15	1.12021	45.766	1.12162	88.086	0.88083	0.464	0.87835	0.801
301.15	1.11860	41.437	1.11996	79.668	0.87867	0.454	0.87638	0.779
305.15	1.11537	34.380	1.11666	65.280	0.87424	0.434	0.87233	0.737
307.15	1.11378	31.341	1.11500	59.406	0.87206	0.425	0.87031	0.717

ESI Mass Spectrometric Analysis. A Mariner ESI-TOF mass spectrometer equipped with an API ion source (Perseptive Biosystems) was used with an orifice potential of 200 V and an ion spray voltage of 5 kV; the obtained mass spectra were processed by the "Data Explorer ver. 3.0" software (Perseptive Biosystems). The PEG samples were dissolved in CH_3OH/H_2O (60/40 by volume) and injected into the source at a flow rate of 7 μL/min.

Density, Kinematic Viscosity, and Refraction Index Measurements. Density values of the pure liquids and liquid mixtures were measured by a vibrating density meter (Anton Paar 60, Graz, Austria) equipped with a measuring cell (model 602). The vibrating tube temperature was regulated to better than ±0.01 K using an external thermostatic bath (Heto, type 01 DBT 623, Birkeròd, Denmark) and a digital thermometer (Anton Paar, type CTK 100) with precision of ±0.01 K. The apparatus was calibrated periodically with double-distilled water and dry air whose values are reported in the literature.[5,6] The measured densities, ρ, dynamic viscosities, η (obtained from the measured kinematic viscosities, ν), and refractive indices, n_D, of the pure components are listed in Tables 1 and 2, together with published literature values.[7−18]

Samples were prepared by mass using airtight stoppered bottles and a digital balance (Mettler, model AE 160, Switzerland) with an accuracy of 1×10^{-4} g. PEG was weighted as the first component in a stoppered bottle. 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.[19] All masses were corrected for buoyancy and evaporation of components. The possible error in the mole fraction was estimated to be less than ±0.0001, and the precision of the measured densities was on the order of $\pm 1.5 \times 10^{-5}$ g·cm^{-3} corresponding to a value of $\pm 3 \times 10^{-3}$ cm^3·mol^{-1} in excess molar volume, V_m^E.

Before measurements, the apparatus was checked by determining V_m^E using the test mixture benzene + cyclohexane at 298.15 K. Our results agree with those of the literature data,[20] showing a discrepancy of ±0.5% in the central range of mole fraction of benzene.

The kinematic viscosities, ν, were determined using several Ubbelohde viscometers with a Schott-Geräte automatic measuring unit (model AVS 350), equipped with a thermostat (Lauda, model E 200, Germany), which provides temperature stabilization with an accuracy of ±0.01 K. Six sets of viscometers with capillary diameters from 0.36 mm up to 1.50 mm were used for kinematic ranges of 0.2 to 60 mm^2·s^{-1}, respectively. The viscometers were filled with 15 cm^3 of solution for each measure. 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%.

The kinematic viscosities were determined according to the equation

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

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. In the whole set of experiments flow times were maintained >200 s by selecting viscometers with appropriate values of k.

Viscosities of PEG 200, PEG 400 + oxolane, and oxane were also measured at (297, 299, 301, 305, and 307) 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 was used, which includes the motor, tachogenerator, calibrated spring, torque transducer, and pre-amplifier. The sensor system (NV type) includes a bell-shaped rotor and a cup inserted into a temperature vessel equipped with a Pt100 thermometric probe. It is classified

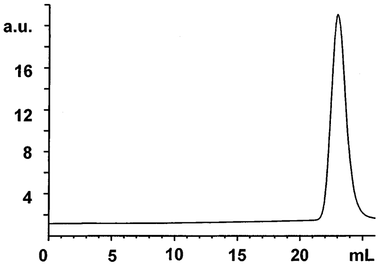

Figure 1. GPC trace of PEG 400.

as a coaxial cylinder sensor system with two gaps for shearing the samples on the inside and on the outside of the rotor. 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 error of ±1.5%. Preliminary tests showed that the investigated specimens display Newtonian behavior at shear rates ranging from (0 to 200) s^{-1}. For each mixture, 9 cm^3 was introduced into the cup at 297.15 K and the viscosity was obtained as the average of 50 measurements at a constant shear rate of 120 s^{-1}. Then, the temperature was increased and allowed to stabilize and the procedure repeated to obtain the next value of the viscosity. The rotary rheometer was preferred over the Ubbelohde viscometers because the overall time to perform experiments at six different temperatures is much shorter. For capillary viscometers such experimental times are substantially longer, leading to biased values of viscosity, likely attributable to a significant evaporation of the highly volatile component. For pure PEG samples, results obtained by capillary and rotary viscometers agreed within the limits of the experimental errors.

The refractive indices, n_D, were measured using a thermostated Abbe refractometer (Carl Zeiss, model G, Jena, Switzerland), which works with the wavelength corresponding to the D line of sodium. The experimental reproducibility in the refractive index data is 1 × 10^{-4}. An average of five measurements was taken for each sample mixture.

Results and Discussion

Polymers are mixtures of macromolecules having different molecular weights and/or chemical compositions (distribution of comonomers, cyclic or open-chain structure and, as in this last case, different types of terminal groups). Thus, for an accurate characterization of a polymeric sample, both the molecular weight distribution (MWD) and the chemical composition are needed.

The MWD is usually determined by such techniques as gel permeation chromatography (GPC), and Figure 1 reports the trace of PEG 400 as an example. From this curve, by the PL-caliber software, different averages can be computed, like the number average, M_n ($=\Sigma N_iM_i/\Sigma N_i$), and the weight average, M_w ($=\Sigma N_iM_i^2/\Sigma N_iM_i = \Sigma w_iM_i$), where N_i is the number of moles of species i, having molecular weight M_i, and weight fraction w_i. Moreover, M_n and M_w can be obtained directly by osmometry and light-scattering measurements, respectively. M_w and M_n normally differ from each other and their ratio, M_w/M_n, allows estimating the polydispersity of a polymer sample, ranging from 1 for monodisperse systems to few hundreds for highly polydisperse systems. In the present work, M_n was used to compute the molar fractions of the solute and, for PEG 200 and 400, the values obtained are $M_n = 192$ with $M_w/M_n = 1.165$ and $M_n = 408$ with $M_w/M_n = 1.096$, respectively.

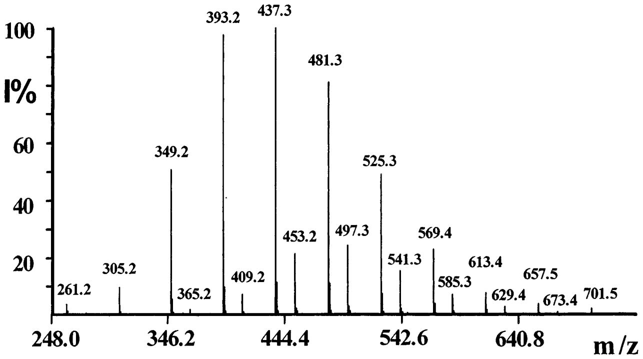

Figure 2. Electrospray mass spectrum of PEG 400.

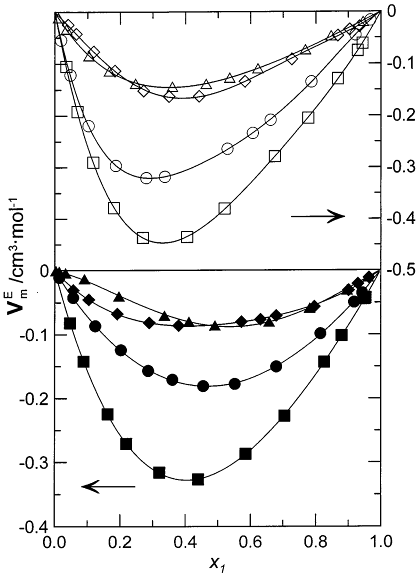

Figure 3. Excess molar volumes, V_m^E, vs the mole fraction, x_1, of PEG 200 + 1,3-dioxolane (●), + 1,4-dioxane (▲), + oxolane (■), + oxane (◆), and of PEG 400 + 1,3-dioxolane (○), + 1,4-dioxane (△), + oxolane (□), + oxane (◇), respectively, at 303.15 K. Full lines correspond to the Redlich–Kister polynomial.

The determination of the purity of polymer specimens is another important issue. Melting point measurements are not suitable tests for assessing their purity because melting takes place over a temperature range. In the present work, we have attempted an accurate characterization of PEGs by ESI mass spectrometry, and in Figure 2, the ESI mass spectrum of a PEG 400 sample is reported as an example. The spectrum is formed by two families of peaks, corresponding to HO−(−CH_2−CH_2−O−)$_n$−H molecules, cationized with Na^+ ($m/z = 41.00 + n\cdot 44.03$ with $n = 5-15$) or with K^+ ($m/z = 56.97 + n\cdot 44.03$ with $n = 7-15$). Peaks at $m/z = 19.02 + n\cdot 44.03$ with $n = 10-14$, due to PEG molecules cationized with H^+, are also found in the spectrum with very low intensity. Thus, the degree of impurities in the investigated PEG samples is negligible, being that all the peaks are present in the mass spectra attributable to PEG molecules.

Experimental densities, ρ, dynamic viscosities, η, refractive indices, n_D, excess molar volumes, V_m^E, deviations in viscosities, $\Delta\eta$, and deviations in molar refraction, ΔR, are reported in Tables 1−4. The excess molar volumes, V_m^E,

Table 3. Densities, ρ, and Excess Molar Volumes, V_m^E, for Binary Mixtures Containing PEG 200 and PEG 400 + Cyclic Ethers at 303.15 K

x_1	ρ ($g\cdot cm^{-3}$)	V_m^E ($cm^3\cdot mol^{-1}$)	x_1	ρ ($g\cdot cm^{-3}$)	V_m^E ($cm^3\cdot mol^{-1}$)
PEG 200 (1) + 1,3-Dioxolane (2)					
0.0141	1.05502	−0.011	0.4548	1.09753	−0.181
0.0565	1.06148	−0.042	0.5515	1.10249	−0.177
0.1240	1.07032	−0.087	0.6794	1.10779	−0.150
0.2029	1.07882	−0.124	0.8142	1.11223	−0.099
0.2859	1.08620	−0.157	0.9175	1.11506	−0.049
0.3599	1.09165	−0.171	0.9424	1.11567	−0.035
PEG 200 (1) + 1,4-Dioxane (2)					
0.0039	1.02319	−0.001	0.4103	1.07812	−0.080
0.0137	1.02501	−0.002	0.4904	1.08535	−0.086
0.0330	1.02852	−0.004	0.6574	1.09804	−0.080
0.0907	1.03828	−0.013	0.7812	1.10580	−0.058
0.1963	1.05383	−0.040	0.8962	1.11203	−0.030
0.3351	1.07051	−0.070	0.9603	1.11517	−0.010
PEG 200 (1) + Oxolane (2)					
0.0471	0.89973	−0.082	0.5854	1.05837	−0.287
0.0884	0.91836	−0.142	0.7046	1.07852	−0.227
0.1622	0.94788	−0.224	0.8261	1.09604	−0.143
0.2191	0.96788	−0.271	0.8799	1.10300	−0.102
0.3201	0.99855	−0.316	0.9500	1.11145	−0.044
0.4394	1.02857	−0.327	0.9530	1.11180	−0.042
PEG 200 (1) + Oxane (2)					
0.0568	0.89767	−0.030	0.6305	1.05653	−0.076
0.1041	0.91562	−0.045	0.6790	1.06574	−0.070
0.1912	0.94576	−0.067	0.7954	1.08620	−0.056
0.2890	0.97566	−0.081	0.9006	1.10275	−0.031
0.3790	1.00014	−0.086	0.9292	1.10697	−0.021
0.5720	1.04473	−0.080	0.9631	1.11184	−0.011
PEG 400 (1) + 1,3-Dioxolane (2)					
0.0187	1.05932	−0.054	0.5284	1.10997	−0.264
0.0474	1.06767	−0.121	0.6065	1.11206	−0.234
0.1026	1.07946	−0.219	0.6612	1.11329	−0.209
0.1865	1.09090	−0.296	0.7860	1.11554	−0.135
0.2794	1.09882	−0.320	0.9215	1.11740	−0.045
0.3361	1.10228	−0.318	0.9672	1.11794	−0.017
PEG 400 (1) + 1,4-Dioxane (2)					
0.0109	1.02682	−0.011	0.4630	1.09842	−0.138
0.0354	1.03568	−0.033	0.5354	1.10261	−0.127
0.1043	1.05487	−0.084	0.6223	1.10678	−0.109
0.1665	1.06729	−0.113	0.7675	1.11220	−0.073
0.2466	1.07910	−0.138	0.8466	1.11456	−0.046
0.3591	1.09073	−0.144	0.9447	1.11709	−0.019
PEG 400 (1) + Oxolane (2)					
0.0343	0.91040	−0.105	0.5197	1.07840	−0.380
0.0688	0.93792	−0.192	0.6744	1.09571	−0.279
0.1171	0.96843	−0.290	0.7762	1.10433	−0.205
0.1806	0.99883	−0.378	0.8676	1.11074	−0.129
0.2695	1.02940	−0.437	0.9283	1.11444	−0.075
0.4046	1.06041	−0.435	0.9433	1.11530	−0.061
PEG 400 (1) + Oxane (2)					
0.0405	0.90772	−0.025	0.4415	1.05707	−0.162
0.0655	0.92517	−0.042	0.5822	1.07933	−0.134
0.1183	0.95605	−0.076	0.7260	1.09612	−0.092
0.1836	0.98611	−0.113	0.8677	1.10883	−0.046
0.2716	1.01687	−0.152	0.9037	1.11160	−0.035
0.3489	1.03755	−0.163	0.9336	1.11381	−0.029

were computed using the following equation,

$$V_m^E = (x_1M_1 + x_2M_2)/\rho - x_1M_1/\rho_1 - x_2M_2/\rho_2 \qquad (2)$$

where x_i, M_i, and ρ_i (i = 1, 2) are the mole fractions, molecular weights, and densities of the pure PEG (component 1) and component 2, respectively. As can be seen from Table 3 and Figure 3, the values of V_m^E are negative for all mixtures, varying in the sequence PEG + oxolane < PEG + 1,3-dioxolane < PEG + oxane < PEG + 1,4-dioxane. For all mixtures, deviation from ideality increases as the PEG molecular weight is increased. The largest deviations in V_m^E are in the range $x_1 \approx 0.25-0.48$.

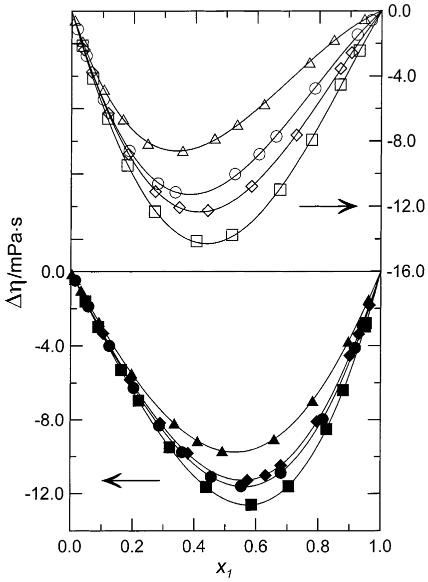

Figure 4. Deviations in viscosity, $\Delta\eta$, vs the mole fraction, x_1, of PEG 200 + 1,3-dioxolane (●), + 1,4-dioxane (▲), + oxolane (■), + oxane (◆), and of PEG 400 + 1,3-dioxolane (○), + 1,4-dioxane (△), + oxolane (□), + oxane (◇), respectively, at 303.15 K. Full lines correspond to the Redlich−Kister polynomial.

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

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \qquad (3)$$

where η, η_1, and η_2 are the viscosities of the mixture and of pure components, respectively. The viscosity deviations, $\Delta\eta$, vs the mole fraction of PEG are plotted in Figure 4. It can be seen that $\Delta\eta$ is negative for all the investigated binary systems, over the whole composition range. Minima are located at $x_1 \approx 0.3-0.6$.

The deviations in molar refraction, ΔR, were calculated from the Lorentz−Lorenz equation,

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

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

$$\varphi_i = x_iV_i / \sum_{i=1}^{2} x_iV_i \qquad (5)$$

where $V_i = M_i/\rho_i$.

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 a binary mixture 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, $V_m = (x_1M_1 + x_2M_2)/\rho$.

Table 4. Dynamic Viscosities, η, Deviations in Viscosities, $\Delta\eta$, Refractive Indices, n_D, and Deviations in Refractive Indices, ΔR, of Binary Mixtures Containing PEG 200, PEG 400 + Cyclic Ethers at 303.15 K

x_1	η (mPa·s)	$\Delta\eta$ (mPa·s)	n_D	ΔR (cm^3·mol^{-1})	x_1	η (mPa·s)	$\Delta\eta$ (mPa·s)	n_D	ΔR (cm^3·mol^{-1})
PEG 200 (1) + 1,3-Dioxolane (2)									
0.0141	0.606	−0.477	1.3985	−0.581	0.4548	6.346	−11.094	1.4381	−6.419
0.0565	0.779	−1.877	1.4041	−2.125	0.5515	9.421	−11.612	1.4428	−5.907
0.1240	1.165	−3.996	1.4124	−3.959	0.6794	14.884	−10.895	1.4481	−4.703
0.2029	1.836	−6.256	1.4203	−5.375	0.8142	22.866	−7.919	1.4524	−2.971
0.2859	2.861	−8.312	1.4272	−6.208	0.9175	30.484	−4.133	1.4552	−1.385
0.3599	4.189	−9.730	1.4325	−6.504	0.9424	32.607	−2.936	1.4558	−0.975
PEG 200 (1) + 1,4-Dioxane (2)									
0.0039	1.118	−0.125	1.4180	−0.098	0.4103	6.955	−9.155	1.4412	−4.263
0.0137	1.174	−0.426	1.4188	−0.330	0.4904	9.349	−9.690	1.4441	−4.173
0.0330	1.297	−1.011	1.4203	−0.767	0.6574	16.105	−9.044	1.4494	−3.376
0.0907	1.713	−2.704	1.4245	−1.875	0.7812	22.723	−6.956	1.4526	−2.379
0.1963	2.802	−5.479	1.4310	−3.278	0.8962	30.117	−3.767	1.4550	−1.221
0.3351	5.184	−8.175	1.4380	−4.148	0.9603	34.729	−1.502	1.4563	−0.480
PEG 200 (1) + Oxolane (2)									
0.0471	0.586	−1.610	1.4236	−7.143	0.5854	9.647	−12.595	1.4528	−22.979
0.0884	0.760	−2.975	1.4268	−10.645	0.7046	15.054	−11.629	1.4570	−19.301
0.1622	1.189	−5.295	1.4331	−16.165	0.8261	22.707	−8.502	1.4600	−13.706
0.2191	1.663	−6.940	1.4391	−20.489	0.8799	26.827	−6.384	1.4623	−6.988
0.3201	2.868	−9.495	1.4451	−23.332	0.9500	32.856	−2.968	1.4628	−5.138
0.4394	5.193	−11.614	1.4491	−23.904	0.9530	33.134	−2.797	1.4631	−3.580
PEG 200 (1) + Oxane (2)									
0.0568	0.997	−1.859	1.4206	−0.837	0.6305	13.029	−11.010	1.4476	−2.559
0.1041	1.276	−3.326	1.4237	−1.409	0.6790	15.387	−10.439	1.4492	−2.327
0.1912	2.007	−5.812	1.4289	−2.202	0.7954	22.038	−8.089	1.4525	−1.632
0.2890	3.262	−8.164	1.4342	−2.735	0.9006	29.480	−4.532	1.4547	−0.877
0.3790	4.936	−9.817	1.4383	−2.970	0.9292	31.691	−3.377	1.4555	−0.622
0.5720	10.572	−11.304	1.4457	−2.772	0.9631	34.440	−1.878	1.4563	−0.331
PEG 400 (1) + 1,3-Dioxolane (2)									
0.0187	0.784	−1.103	1.4029	−5.932	0.5284	28.063	−10.128	1.4547	−27.136
0.0474	1.188	−2.745	1.4129	−13.088	0.6065	34.950	−8.803	1.4570	−23.581
0.1026	2.334	−5.534	1.4226	−22.542	0.6612	39.930	−7.714	1.4567	−21.013
0.1865	5.244	−8.594	1.4274	−30.262	0.7860	51.722	−4.814	1.4609	−13.689
0.2794	9.853	−10.606	1.4428	−32.456	0.9215	64.595	−1.594	1.4629	−5.190
0.3361	13.366	−11.131	1.4463	−32.438	0.9672	68.862	−0.575	1.4635	−2.182
PEG 400 (1) + 1,4-Dioxane (2)									
0.0109	1.304	−0.563	1.4180	−0.098	0.4630	25.968	−7.891	1.4412	−4.263
0.0354	1.745	−1.857	1.4188	−0.330	0.5354	31.995	−6.988	1.4441	−4.173
0.1043	3.663	−4.816	1.4203	−0.767	0.6223	39.509	−5.628	1.4494	−3.376
0.1665	6.227	−6.652	1.4245	−1.875	0.7675	52.363	−3.048	1.4526	−2.379
0.2466	10.445	−8.102	1.4310	−3.278	0.8466	59.266	−1.743	1.4550	−1.221
0.3591	17.920	−8.587	1.4380	−4.148	0.9447	67.450	−0.497	1.4563	−0.480
PEG 400 (1) + Oxolane (2)									
0.0343	0.765	−2.125	1.4117	−8.181	0.5197	23.769	−13.745	1.4544	−24.747
0.0688	1.213	−4.140	1.4191	−14.303	0.6744	37.570	−10.982	1.4586	−18.269
0.1171	2.183	−6.610	1.4273	−20.328	0.7762	47.889	−7.927	1.4607	−13.057
0.1806	3.836	−9.489	1.4354	−25.168	0.8676	57.812	−4.526	1.4620	−7.973
0.2695	7.350	−12.318	1.4426	−28.213	0.9283	64.213	−2.448	1.4629	−4.391
0.4046	15.175	−14.131	1.4503	−27.742	0.9433	65.808	−1.925	1.4632	−3.468
PEG 400 (1) + Oxane (2)									
0.0405	1.252	−2.383	1.4236	−7.143	0.4415	19.902	−12.250	1.4528	−22.979
0.0655	1.676	−3.740	1.4268	−10.645	0.5822	31.380	−10.774	1.4570	−19.301
0.1183	2.887	−6.280	1.4331	−16.165	0.7260	44.774	−7.606	1.4600	−13.706
0.1836	5.022	−8.790	1.4391	−20.489	0.8677	58.908	−3.541	1.4623	−6.988
0.2716	8.981	−11.089	1.4451	−23.332	0.9037	62.434	−2.576	1.4628	−5.138
0.3489	13.506	−12.059	1.4491	−23.904	0.9336	65.371	−1.770	1.4631	−3.580

The molar refraction and molar refraction deviation, ΔR, were calculated with an accuracy of ±0.0001 cm^3·mol^{-1}. The deviations in refractive indices are shown in Figure 5. The ΔR values are negative for all mixtures in the whole composition range, showing values larger than those obtained for V^E_m and $\Delta\eta$ and a stronger dependence on PEG molecular weight.

The variation of V^E_m, $\Delta\eta$, and ΔR with composition are expressed by the Redlich−Kister polynomial

$$Q^E_m = x_1 x_2 \sum_{k\geq 0} a_k (x_1 - x_2)^k \tag{8}$$

where Q^E_m refers to V^E_m, $\Delta\eta$, and ΔR.

The adjustable parameters a_k were determined by fitting the experimental values to eq 8 with the least-squares methods and the results are given in Table 5. The tabulated standard deviations, $\sigma(Q^E_m)$ reported in Table 6 were defined as

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

with N and n as the number of experimental points and parameters, respectively, whereas ϕ_{min} is the minimum value of the objective function ϕ defined as

$$\phi = \sum_{k=1}^{N} {\eta_k}^2 \tag{10}$$

where $\eta_k = Q^E_{m,calcd} - Q^E_m$; Q^E_m is the experimental value and $Q^E_{m,calcd}$ is evaluated through eq 8. The full lines in Figures 3−5 correspond to the Redlich−Kister polynomials.

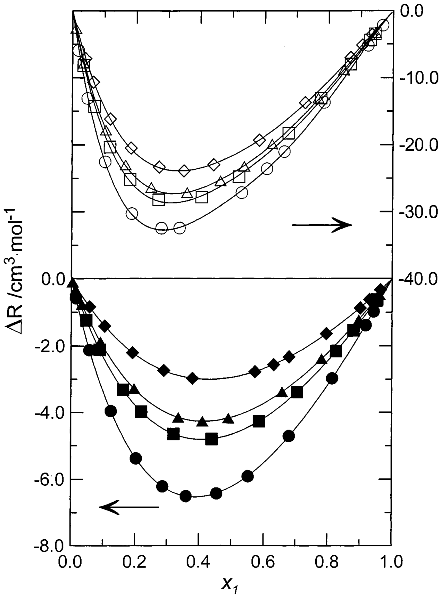

Figure 5. Deviations in refractive indices, ΔR, vs the mole fraction, x_1, of PEG 200 + 1,3-dioxolane (●), + 1,4-dioxane (▲), + oxolane (■), + oxane (◆), and of PEG 400 + 1,3-dioxolane (○), + 1,4-dioxane (△), + oxolane (□), + oxane (◇), respectively, at 303.15 K. Full lines correspond to the Redlich−Kister polynomial.

Table 5. Least-Squares Parameters, a_k, Eq 8, and Standard Deviations, $\sigma(Q_m^E)$ of Binary Mixtures Containing PEG 200 and PEG 400 + Cyclic Ethers at 303.15 K

function	a_0	a_1	a_2	a_3	$\sigma(Q_m^E)$
PEG 200 (1) + 1,3-Dioxolane (2)					
V_m^E (cm³·mol⁻¹)	−0.7213	0.0911			0.0011
$\Delta\eta$ (mPa·s)	−45.7911	−11.8707	1.0056	1.2825	0.0157
ΔR (cm³·mol⁻¹)	−24.874	10.460	−4.8699	2.2606	0.0089
PEG 200 (1) + 1,4-Dioxane (2)					
V_m^E (cm³·mol⁻¹)	−0.3484	−0.0749	0.1553		0.0012
$\Delta\eta$ (mPa·s)	−38.8699	−5.3312	3.3024	1.0446	0.0080
ΔR (cm³·mol⁻¹)	−16.566	5.5444	−1.9240	0.6191	0.0036
PEG 200 (1) + Oxolane (2)					
V_m^E (cm³·mol⁻¹)	−1.2633	0.4892	−0.1325		0.0008
$\Delta\eta$ (mPa·s)	−49.2361	−15.9297	0.0601	1.6178	0.0114
ΔR (cm³·mol⁻¹)	−18.6241	6.5738	−2.3572	1.0585	0.0084
PEG 200 (1) + Oxane (2)					
V_m^E (cm³·mol⁻¹)	−0.3374	0.0857	−0.1256		0.0017
$\Delta\eta$ (mPa·s)	−44.5079	−10.9117	2.0274	2.2076	0.0135
ΔR (cm³·mol⁻¹)	−11.759	3.2988	−0.9779	0.2181	0.0078
PEG 400 (1) + 1,3-Dioxolane (2)					
V_m^E (cm³·mol⁻¹)	−1.1027	0.6984	−0.6600	0.6068	0.0009
$\Delta\eta$ (mPa·s)	−42.1272	24.3427	1.7203	−1.5593	0.0651
ΔR (cm³·mol⁻¹)	−111.24	71.405	−74.570	60.383	0.31
PEG 400 (1) + 1,4-Dioxane (2)					
V_m^E (cm³·mol⁻¹)	−0.5304	0.3072	−0.1539	0.0591	0.0013
$\Delta\eta$ (mPa·s)	−29.9873	25.0341	−2.9348		0.0534
ΔR (cm³·mol⁻¹)	−96.798	58.019	−47.307	34.390	0.20
PEG 400 (1) + Oxolane (2)					
V_m^E (cm³·mol⁻¹)	−1.5697	1.0946	−0.6818		0.0010
$\Delta\eta$ (mPa·s)	−56.0970	16.2423	6.8714		0.077
ΔR (cm³·mol⁻¹)	−100.558	61.999	−54.107	37.812	0.27
PEG 400 (1) + Oxane (2)					
V_m^E (cm³·mol⁻¹)	−0.6175	0.3986	0.0726	−0.3259	0.0017
$\Delta\eta$ (mPa·s)	−47.6198	19.5867	3.6642	−0.3593	0.0408
ΔR (cm³·mol⁻¹)	−86.384	48.754	−36.347	23.246	0.13

Table 6. Coefficients of McAllister's Models and Standard Deviations for Kinematic Viscosities at 303.15K

three-body model			four-body model			
ν_{12}	ν_{21}	σ (10^{-6} m² s⁻¹)	ν_{1112}	ν_{1122}	ν_{2221}	σ (10^{-6} m² s⁻¹)
PEG 200 (1) + 1,3-Dioxolane (2)						
15.793	4.646	0.010	17.944	9.384	4.688	0.006
PEG 200 (1) + 1,4-Dioxane (2)						
18.219	5.934	0.006	20.355	11.097	6.348	0.003
PEG 200 (1) + Oxolane (2)						
15.103	4.062	0.010	17.442	8.572	4.250	0.006
PEG 200 (1) + Oxane (2)						
17.264	4.749	0.014	18.751	10.421	4.958	0.009
PEG 400 (1) + 1,3-Dioxolane (2)						
24.377	95.628	0.086	60.255	15.561	118.545	0.033
PEG 400 (1) + 1,4-Dioxane (2)						
30.785	73.138	0.062	56.546	22.118	91.038	0.015
PEG 400 (1) + Oxolane (2)						
26.529	66.127	0.081	53.224	15.735	84.879	0.024
PEG 400 (1) + Oxane (2)						
31.911	52.322	0.048	50.704	22.400	61.885	0.007

The McAllister's multibody interaction model,[21] widely used to correlate the kinematic viscosity of liquid mixtures with mole fraction, was applied to our data. We used the three-body model defined as

$$\begin{aligned}\ln \nu = {} & x_1^3 \ln \nu_1 + 3x_1^2x_2 \ln \nu_{12} + \\ & 3x_1x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 - \ln(x_1 + x_2M_2/M_1) + \\ & 3x_1^2x_2 \ln\,[(2 + M_2/M_1)/3] + 3x_1x_2^2 \ln\,[(1 + 2M_2/M_1)/3] + \\ & x_2^3 \ln(M_2/M_1) \end{aligned} \quad (11)$$

and the four-body model given by

$$\begin{aligned}\ln \nu = {} & x_1^4 \ln \nu_1 + 4x_1^3x_2 \ln \nu_{1112} + 6x_1^2x_2^2 \ln \nu_{1122} + \\ & 4x_1x_2^3 \ln \nu_{2221} + x_2^4 \ln \nu_2 - \ln(x_1 + x_2M_2/M_1) + \\ & 4x_1^3x_2 \ln[(3 + M_2/M_1)/4] + 6x_1^2x_2^2 \ln[(1 + M_2/M_1)/2] + \\ & 4x_1x_2^3 \ln[(1 + 3M_2/M_1)/4] + x_2^4 \ln(M_2/M_1) \end{aligned} \quad (12)$$

where ν_{12}, ν_{21}, ν_{1112}, ν_{1122}, and ν_{2221} are the model parameters. Table 6 records the calculated results, showing that both models are in agreement with experimental data.

When possible, the viscosity of binary solutions was also measured by the rotary rheometer. Table 7 reports values of η at different temperatures for these solutions. Values of η vs T have been correlated by an Arrhenius-type equation,

$$\eta = A \exp\left(\frac{E_{att}}{RT}\right) \quad (13)$$

where A and E_{att} are adjustable parameters and R is the ideal gas constant. Because all the investigated mixtures display Newtonian behavior, E_{att} can be interpreted, according to Eyring's model for viscous flow, as the activation energy related to molecular jumps under the effect of the applied shear stress. For binary mixtures of PEG 400 with oxolane and oxane, values of E_{att} are similar (Table 7). This suggests that, for $x_1 > 0.5$, the segment motions of the polymer chains control the shear flow dynamics.

Conclusions

Values of V_m^E, $\Delta\eta$, and ΔR are negative for all mixtures. As reported in Figure 3, mixtures of PEG with 1,4-dioxane and oxane display values of V_m^E that are similar in the whole composition range and consistently above the corresponding values of other mixtures. In contrast, it is of

Table 7. Viscosities, η, at Different Temperatures and Compositions of Solutions of PEG 400, Oxolane, and Oxane; Activation Energies for Viscous Flow, E_{att}, Computed by Eq 13

	η (mPa·s)					
x_1	T = 297.15 K	T = 299.15 K	T = 301.15 K	T = 305.15 K	T = 307.15 K	E_{att} (kJ·mol^{-1})
			PEG 400 (1) + Oxolane (2)			
0.0000	0.473	0.464	0.454	0.434	0.425	8.20
0.6744	48.96	45.04	41.81	35.43	32.74	30.78
0.7762	64.54	59.08	53.87	45.23	41.50	33.91
0.8676	79.56	72.31	65.80	55.35	50.29	34.98
0.9283	88.48	80.22	72.43	60.08	54.26	37.22
0.9433	90.84	82.32	74.63	61.63	55.81	37.19
1.0000	97.909	88.086	79.668	65.280	59.406	37.96
			PEG 400 (1) + Oxane (2)			
0.0000	0.824	0.801	0.779	0.737	0.717	10.61
0.5822	40.66	37.05	34.15	29.15	27.25	30.42
0.7260	59.95	54.26	49.30	40.69	37.19	36.29
0.8677	80.01	72.46	66.14	55.05	50.79	34.84
0.9037	85.17	76.96	69.59	57.66	52.78	36.52
0.9336	90.05	81.10	73.28	60.34	54.85	37.74

interest to note that $\Delta\eta$ of mixtures with 1,3-dioxolane increases above that of oxane mixtures as the PEG molecular weight is increased. With the above-mentioned exception, mixtures with 1,3-dioxolane and oxolane (five-atom ring ethers) display values of V_m^E, $\Delta\eta$, and ΔR that are always below the corresponding mixtures with six-atom ring ethers. Attempts to explain these trends by changes in dispersion and dipolar forces did not lead to reliable correlations. In fact, dipole moments reported in the literature show significant discrepancies among values of different authors.

However, values of $\Delta\eta$ in Figure 4 can be discussed in terms of changes in the H-bonds among PEG molecules as cyclic ethers are mixed with the polymers. Correlations have been reported between $\Delta\eta$ and the energy and the extent of H-bonds in liquid systems.[22] Accordingly, $\Delta\eta$ decreases as the number and strength of H-bonds are decreased.

Terminal hydroxyl groups of PEG can give head-to-tail connections because they possess both donor and acceptor characteristics. Actually, the solid-state structure of ethylene glycol[23] shows the existence of a three-dimensional network of H-bonds. Moreover, crystallographic data on α,ω-alkanediols confirm the presence of O−H···O chains at both ends of the molecules.[24] These data suggest that extended H-bond supramolecular configurations among PEG molecules are present, to some extent, in the liquid state. Addition of cyclic ethers can perturb such end-to-tail connections because their O-atoms can only act as acceptors. Actually, extended Hückel computations on isolated molecules of the cyclic ethers show that O-atoms bear a significant negative fractional charge (ranging from −0.869 to −0.884). Thus, negative values of $\Delta\eta$ can be attributed to the partial disruption of the cooperative H-bond configurations of PEG that is especially effective when monoethers are added to the polymer.

Inspection of Figures 3−5 shows that minima of V_m^E, $\Delta\eta$, and ΔR move toward smaller values of x_1 as the molecular weight of PEG is increased. Moreover, the minima for mixtures with PEG 400 are more negative. These trends can be related to the decrease of the hydroxyl group fraction with respect to the total number of atoms in the polymer chain as the molecular weight is increased.

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