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Densities, Viscosities, Refractive Indices, and Excess Molar Enthalpies of Binary Mixtures Containing Poly(ethylene glycol) 200 and 400 + Dimethoxymethane and + 1,2-Dimethoxyethane at 298.15 K

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Densities, ρ, viscosities, η, refractive indices, n_D, and excess molar enthalpies, H_m^E, of poly(ethylene glycol) 200 and 400 + dimethoxymethane and + 1,2-dimethoxyethane were determined over the entire range of composition, at 298.15 K and at atmospheric pressure. Excess molar volumes, V_m^E, viscosity deviations, $\Delta\eta$, deviations in molar refractions, ΔR, and excess molar enthalpies, H_m^E, were evaluated from experimental data. Deviations are negative with the exception of those of H_m^E, which are all positive. The excess or bulk properties were fitted to the Redlich−Kister polynomial to estimate the binary interaction parameters. The McAllister multibody interaction model was used to correlate the kinematic viscosities of liquid mixtures with mole fractions.

Introduction

Poly(ethylene glycols) (PEGs) have received increasing attention as a class of chemical substances widely used in different industrial applications. Actually, PEG’s low toxicity has favored its usage in the pharmaceutical, cosmetic,[1] food, and textile fields.[2] Moreover, in recent years, attention has been focused on the solubility of PEG in both water and organic solvents, a valuable property in the development of more environmental friendly processes, like the design of water soluble catalysts, and in the extraction, separation, and purification of biological substances.[3−5] Thus, evaluation of thermodynamic and bulk properties of PEGs and their mixtures with organic solvents may prove quite relevant to the design and implementation of the above-mentioned processes, especially for the establishment of reliable correlations and predictions.

In a previous paper[6] we studied binary mixtures containing PEG 200 and 400 + four cyclic ethers. In the present paper we have continued our study and we have determined densities, viscosities, refractive indices, and excess molar enthalpies of mixtures containing PEG 200 and 400 + two aliphatic ethers, namely dimethoxymethane and 1,2-dimethoxyethane, respectively. Investigations were not extended to linear ethers of longer chains, since PEG is only partially soluble in these systems and the corresponding solutions show the presence of two distinct liquid phases. No data have been found in the literature on the mixtures studied in this paper.

Experimental Section

Materials. PEG 200 and 400, purchased from Fluka, were used without further purification. As previously reported,[6] molecular weights were obtained by gel permeation chromatography (GPC). Both the number average, M_n ($=\sum N_iM_i/\sum N_i$), and the 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 weight M_i and weight fraction w_i. A polydispersity index was obtained as the ratio M_w/M_n. 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. The purity of the PEG samples was tested by ESI mass spectrometry. The degree of impurities was negligible, since all the peaks present in the mass spectra are attributable to PEG molecules.[6] Dimethoxymethane and 1,2-dimethoxyethane were from Aldrich with purities >99% and >99.9%, respectively. All chemicals were used without further purification, degassed by ultrasound (ultrasonic bath, Hellma, type 460, Milan, Italy), kept in dark bottles, and dried over molecular sieves (Union Carbide, Type 4A, $^1/_{16}$ in. pellets) to reduce the water content.

Density and Refractive Index Measurements. Binary mixtures were prepared by mass using a digital balance (Mettler, model AE 160, Switzerland), covering the whole composition range of the mixtures. Precautions were taken such as using samples recently prepared, reducing to a minimum the vapor space in the vessels, according to the procedure described elsewhere.[7] PEG was weighted as first component. The accuracy in the determination of mole fraction of the measured samples was $\pm 10^{-4}$.

Values of density, ρ, of the pure liquids and liquid mixtures were measured by means of 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) with a digital thermometer (Anton Paar, type CTK 100), showing an uncertainty of ±0.01 K. The

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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 at 298.15 K

	ρ/g·cm^{-3}		η/mPa·s		n_D	
compound	this work	lit.	this work	lit.	this work	lit.
PEG 200	1.120 96	1.120 98[6]	48.097	48.157[6]	1.4585	1.4585[6]
PEG 400	1.122 49	1.122 30[16]	92.663	92.797[6]	1.4650	1.4650[6]
dimethoxymethane	0.855 73	0.856 54[17]	0.312		1.3513	1.35132[12]
1,2-dimethoxyethane	0.861 26	0.861 90[18] 0.861 29[19]	0.414	0.455[12] 0.417[20] 0.412[21]	1.3778	1.37811[12]

Table 2. Densities, ρ, and Excess Molar Volumes, V_m^E, for Binary Mixtures Containing PEG 200 and PEG 400 + Dimethoxymethane and + 1,2-Diethoxyethane at 298.15 K

x_1	ρ / g·cm^{-3}	V_m^E / cm^3·mol^{-1}	x_1	ρ / g·cm^{-3}	V_m^E / cm^3·mol^{-1}
PEG 200 (1) + Dimethoxymethane (2)					
0.0431	0.879 84	−0.306	0.5093	1.041 70	−1.153
0.0920	0.904 42	−0.574	0.6030	1.061 40	−1.045
0.1479	0.929 57	−0.803	0.7221	1.082 67	−0.807
0.2072	0.953 33	−0.976	0.7779	1.091 47	−0.665
0.2694	0.975 48	−1.095	0.8950	1.107 89	−0.316
0.3779	1.008 70	−1.186	0.9534	1.115 30	−0.136
PEG 200 (1) + 1,2-Dimethoxyethane (2)					
0.0586	0.887 38	−0.313	0.5911	1.050 13	−0.891
0.1097	0.908 65	−0.521	0.6939	1.070 90	−0.736
0.2018	0.943 17	−0.783	0.7958	1.089 28	−0.524
0.3011	0.975 69	−0.939	0.8707	1.101 57	−0.338
0.4174	1.008 79	−0.998	0.9285	1.110 49	−0.186
0.4981	1.029 07	−0.976	0.9648	1.115 87	−0.092
PEG 400 (1) + Dimethoxymethane (2)					
0.0348	0.893 41	−0.384	0.4902	1.074 52	−1.278
0.0758	0.928 96	−0.740	0.5423	1.082 24	−1.190
0.1294	0.964 79	−1.068	0.6245	1.092 56	−1.020
0.1963	0.998 20	−1.318	0.7257	1.102 87	−0.774
0.2501	1.018 72	−1.414	0.8576	1.113 46	−0.404
0.3688	1.051 64	−1.427	0.9201	1.117 66	−0.220
PEG 400 (1) + 1,2-Dimethoxyethane (2)					
0.0743	0.922 47	−0.576	0.5072	1.070 18	−1.057
0.1245	0.953 51	−0.845	0.6241	1.087 32	−0.839
0.1958	0.987 92	−1.091	0.6735	1.093 41	−0.740
0.2832	1.019 35	−1.218	0.7546	1.102 25	−0.575
0.4318	1.056 43	−1.169	0.8560	1.111 65	−0.359
0.4321	1.056 50	−1.169	0.9394	1.118 26	−0.163

apparatus was calibrated periodically with double-distilled water and dry air, whose density values are reported in the literature.[8,9] The accuracy in densities was better than $\pm1.5 \times 10^{-5}$ g·cm^{-3}, corresponding to an accuracy of $\pm3 \times 10^{-3}$ cm^3·mol^{-1} in excess molar volumes, V_m^E. All masses were corrected for buoyancy and evaporation of the components, and all molar quantities were based on the relative atomic mass table by IUPAC.[10] 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 found in the literature, showing an uncertainty of ±0.5% in the central range of the mole fraction of benzene.[11]

Refractive indices at the sodium D-line, n_D, were measured using a thermostated Abbe refractometer (Carl Zeiss, model G, Jena, Switzerland) with uncertainty less than ±0.0001 units. Water was circulated into the prism of the refractometer by a circulation pump connected to an external thermostated water bath, with uncertainty ±0.01 K. Calibration was performed by measuring the refractive indices of doubly-distilled water, toluene, cyclohexane, and carbon tetrachloride at defined temperatures.[12] The sample mixtures were directly injected into the prism assembly of the instrument using an airtight hypodermic syringe, and an average of four measurements was taken for each mixture.

Viscosity Measurements. The viscosities of the mixtures and the pure liquids were determined from the flow times in Ubbelohde viscometers by a Schott Geräte AVS 310 unit, equipped with a thermostatic bath (Lauda, model E 200, Germany) which provides temperature stabilization within ±0.01 K. Six sets of Ubbelohde viscometers with capillary diameters from 0.36 up to 1.50 mm were used for the kinematic ranges (0.2 to 60) mm^2·s^{-1}, respectively. Calibration of the viscometers was carried out with double-distilled water. The viscometers were filled with 15 cm^3 of solution, and five runs, at least, were performed for each sample. Flow times were reproducible within ±0.06%, and the uncertainty in the viscosity measurements is ±0.5%.

The kinematic viscosities, ν, were determined according to the equation

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

where t is the experimental flow time, θ is the kinetic energy correction, and k is the viscometer constant, determined by calibration. The absolute (dynamic) viscosity, η, was calculated from the density by the relation $\eta = \nu\rho$.

Calorimetric Measurements. Excess molar enthalpies, H_m^E, have been determined using a flow microcalorimeter (LKB, model 2107, Producer AB, Bromma, Sweden) operating under constant flow conditions. Details and the operating procedure have been described previously.[13,14] Two automatic burets (ABU, Radiometer, Copenhagen, Denmark) have been used to pump continuously, at given rates, the required amounts of pure liquids into the mixing cell. The volume of the cylinder was 2.5 cm^3. Mole fractions were computed from fluxes, and the flow rates were selected to cover the entire mole fraction range. The accuracy of the LKB bath temperature was 0.01 K. The experimental uncertainties in H_m^E and mole fraction, x_1, of PEG were estimated to be <1% and 2×10^{-4}, respectively. The reliability of the calorimeter and the procedure adopted was checked by performing H_m^E measurements on the test system cyclohexane + hexane. Agreement with literature data[15] is better than 0.5% at the maximum of the thermal effect.

Results and Discussion

The measured values of ρ, η, and n_D of pure components, compared with literature values,[6,12,16−21] are listed in Table 1. Tables 2−4 report experimental densities, dynamic viscosities, refractive indices, excess molar volumes, V_m^E, deviations in viscosities, $\Delta\eta$, deviations in molar refraction, ΔR, and excess molar enthalpies, H_m^E, of the solutions under test.

The excess molar volumes were computed by the following equation

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

where x_i, M_i, and ρ_i (i = 1, 2) are the mole fractions, molecular weights, and densities of pure PEG (component

Table 3. Dynamic Viscosities, η, Deviations in Viscosities, $\Delta\eta$, Refractive Indices, n_D, and Deviations in Refractive Indices, ΔR, for Binary Mixtures Containing PEG 200 and PEG 400 + Dimethoxymethane and + 1,2-Diethoxyethane at 298.15 K

x_1	η/mPa·s	$\Delta\eta$/mPa·s	n_D	ΔR/cm^3·mol^{-1}
PEG 200 (1) + Dimethoxymethane (2)				
0.0431	0.417	−1.957	1.3618	−0.970
0.0920	0.573	−4.135	1.3727	−1.866
0.1479	0.827	−6.552	1.3829	−2.722
0.2072	1.220	−8.995	1.3933	−3.360
0.2694	1.775	−11.409	1.4031	−3.806
0.3779	3.247	−15.121	1.4156	−4.276
0.5093	6.382	−18.265	1.4291	−4.147
0.6030	9.906	−19.221	1.4378	−3.675
0.7221	16.566	−18.250	1.4444	−2.967
0.7779	20.871	−16.613	1.4476	−2.488
0.8950	32.892	−10.185	1.4540	−1.257
0.9534	40.769	−5.100	1.4567	−0.575
PEG 200 (1) + 1,2-Dimethoxyethane (2)				
0.0586	0.571	−2.635	1.3862	−0.774
0.1097	0.768	−4.875	1.3931	−1.317
0.2018	1.238	−8.798	1.4042	−2.048
0.3011	2.087	−12.683	1.4146	−2.523
0.4174	3.739	−16.580	1.4250	−2.739
0.4981	5.529	−18.635	1.4312	−2.710
0.5911	8.497	−20.101	1.4376	−2.509
0.6939	13.421	−20.078	1.4440	−2.095
0.7958	20.861	−17.499	1.4495	−1.530
0.8707	28.532	−13.398	1.4532	−1.018
0.9285	36.170	−8.518	1.4558	−0.581
0.9648	41.844	−4.574	1.4573	−0.292
PEG 400 (1) + Dimethoxymethane (2)				
0.0348	0.542	−2.980	1.3750	−7.174
0.0758	0.975	−6.340	1.3859	−14.014
0.1294	1.847	−10.413	1.4026	−19.831
0.1963	3.527	−14.916	1.4143	−24.424
0.2501	5.583	−17.823	1.4247	−26.174
0.3688	11.659	−22.715	1.4372	−27.020
0.4902	21.090	−24.494	1.4465	−24.674
0.5423	26.292	−24.100	1.4494	−23.054
0.6245	35.740	−22.244	1.4538	−19.849
0.7257	49.017	−18.314	1.4576	−15.242
0.8576	68.617	−10.895	1.4621	−8.227
0.9201	78.803	−6.478	1.4646	−4.505
PEG 400 (1) + 1,2-Dimethoxyethane (2)				
0.0743	1.050	−6.214	1.3990	−10.934
0.1245	1.772	−10.125	1.4099	−15.669
0.1958	3.236	−15.245	1.4216	−19.949
0.2832	6.213	−20.325	1.4322	−22.436
0.4318	14.199	−26.050	1.4443	−22.294
0.4321	14.238	−26.040	1.4443	−22.292
0.5072	19.991	−27.209	1.4489	−20.808
0.6241	31.565	−26.423	1.4544	−17.288
0.6735	37.480	−25.067	1.4563	−15.455
0.7546	49.385	−20.643	1.4592	−12.070
0.8560	65.453	−13.930	1.4622	−7.341
0.9394	80.671	−6.404	1.4642	−3.131

1) and component 2, respectively. Figure 1 shows the plots of V_m^E versus the mole fraction, x_1, of PEGs.

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

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \tag{3}$$

where η, η_1, and η_2 are the viscosities of the mixture and of the pure components, respectively. The viscosity deviations, $\Delta\eta$, versus the mole fraction of PEG are plotted in Figure 2. It can be seen that $\Delta\eta$ is negative for all the investigated binary systems, over the whole composition range.

The molar refraction deviations, ΔR, were calculated from the Lorentz−Lorenz equation[22]

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

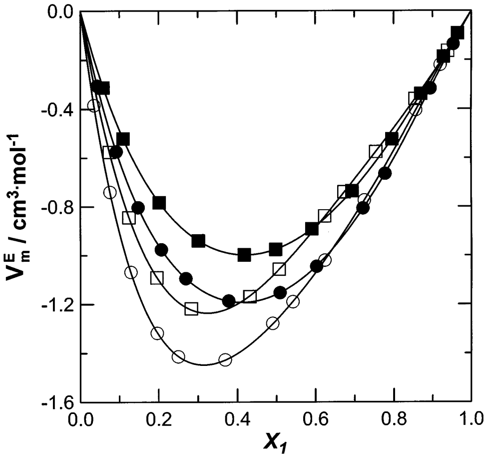

Figure 1. Excess molar volumes, V_m^E, vs the mole fraction, x_1, of PEG 200 + dimethoxymethane (●), PEG 200 + 1,2-dimethoxyethane (■), PEG 400 + dimethoxymethane (○), and PEG 400 + 1,2-dimethoxyethane (□) at 298.15 K. Full lines correspond to the Redlich−Kister polynomial.

Table 4. Excess Molar Enthalpies, H_m^E, for Binary Mixtures Containing PEG 200 and PEG 400 + Dimethoxymethane and + 1,2-Diethoxyethane at 298.15 K

x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}
PEG 200 (1) + Dimethoxymethane (2)					
0.0212	140.0	0.2065	700.2	0.6755	466.9
0.0416	256.0	0.2575	733.9	0.7574	339.2
0.0611	348.5	0.3423	737.8	0.8063	247.7
0.0798	426.4	0.4384	706.8	0.8620	159.3
0.1151	534.9	0.5100	650.7	0.9259	61.0
0.1478	612.9	0.6095	555.3		
PEG 200 (1) + 1,2-Dimethoxyethane (2)					
0.0248	67.0	0.2340	403.7	0.7097	248.7
0.0484	126.5	0.2894	429.0	0.7857	201.1
0.0710	176.0	0.3793	431.7	0.8302	160.2
0.0924	220.8	0.4782	393.3	0.8800	130.0
0.1325	290.3	0.5500	351.3	0.9362	79.1
0.1692	339.8	0.6470	288.8		
PEG 400 (1) + Dimethoxymethane (2)					
0.0101	69.2	0.1092	479.9	0.4951	490.9
0.0200	130.1	0.1405	534.2	0.5954	435.4
0.0297	185.0	0.1969	581.9	0.6623	381.3
0.0393	235.0	0.2689	575.3	0.7464	297.3
0.0601	332.2	0.3290	559.5	0.8548	147.1
0.0756	384.4	0.4238	518.2	0.8983	87.0
PEG 400 (1) + 1,2-Dimethoxyethane (2)					
0.0119	40.3	0.1259	262.4	0.5353	270.3
0.0234	75.2	0.1610	297.1	0.6334	227.6
0.0347	106.9	0.2236	317.4	0.6973	199.1
0.0458	134.6	0.3016	330.7	0.7756	145.5
0.0672	180.6	0.3654	316.8	0.8736	73.0
0.0876	218.4	0.4635	297.3	0.9120	45.1

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

$$\varphi_i = x_i V_i / \sum_{i=1}^{2} x_i V_i \tag{5}$$

where $V_i = M_i/\rho_i$.

The molar refraction, R_i, was obtained from the formula (Lorentz−Lorenz)[23,24]

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

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

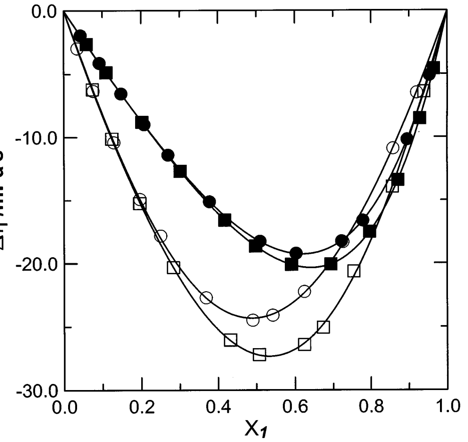

Figure 2. Deviations in viscosity, $\Delta\eta$, vs the mole fraction, x_1, of PEG 200 + dimethoxymethane (●), PEG 200 + 1,2-dimethoxyethane (■), PEG 400 + dimethoxymethane (○), and PEG 400 + 1,2-dimethoxyethane (□) at 298.15 K. Full lines correspond to the Redlich−Kister polynomial.

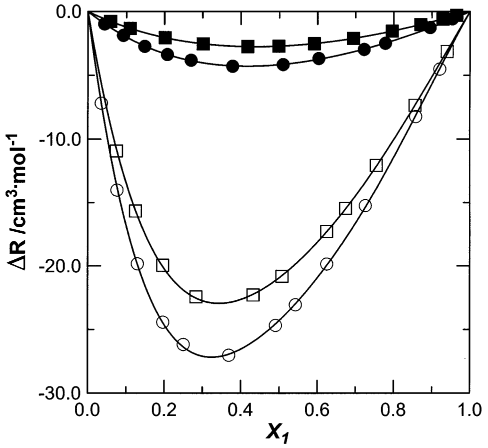

Figure 3. Deviations in refractive indices, ΔR, vs the mole fraction, x_1, of PEG 200 + dimethoxymethane (●), PEG 200 + 1,2-dimethoxyethane (■), PEG 400 + dimethoxymethane (○), and PEG 400 + 1,2-dimethoxyethane (□) at 298.15 K. Full lines correspond to the Redlich−Kister polynomial.

Thus, the equation for binary mixtures becomes

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

where $n_{D(m)}$ is the refractive index of the mixture, $V_m = (x_1M_1 + x_2M_2)/\rho$. Both R_m and ΔR were calculated with an accuracy of ±0.0001 $cm^3 \cdot mol^{-1}$. Figure 3 reports values of ΔR versus the composition of the binary mixtures. PEG 400 mixtures display values of ΔR that are more negative than those for mixtures with PEG 200.

Values of H^E_m were obtained directly from calorimetric measurements and are plotted in Figure 4 against the molar fractions of PEGs.

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

$$Q^E_m = x_1x_2\sum_{k\geq 0} a_k/(x_1 - x_2)^k \tag{8}$$

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

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

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

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

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

where $\xi_k = Q^E_{m,calcd} - Q^E_m$. Q^E_m is the experimental value, and $Q^E_{m,calcd}$ is evaluated through eq 8. The full lines in Figures 1−4 correspond to the Redlich−Kister polynomials.

The McAllister's multibody interaction model,[25] widely used to correlate the kinematic viscosity of liquid mixtures

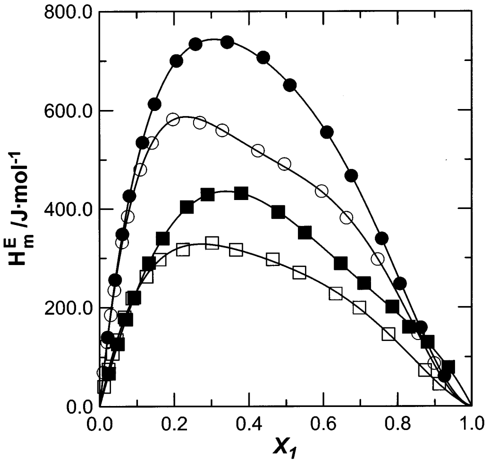

Figure 4. Excess molar enthalpies, H^E_m, vs the mole fraction, x_1, of PEG 200 + dimethoxymethane (●), PEG 200 + 1,2-dimethoxyethane (■), PEG 400 + dimethoxymethane (○), and PEG 400 + 1,2-dimethoxyethane (□) at 298.15 K. Full lines correspond to the Redlich−Kister polynomial.

Table 5. Least-Squares Parameters, a_k, from Eq 8 and Standard Deviations, $\sigma(Q^E_m)$, of Binary Mixtures Containing PEG 200 and PEG 400 + Dimethoxymethane and + 1,2-Diethoxyethane at 298.15 K

function	a_0	a_1	a_2	a_3	$\sigma(Q^E_m)$
	PEG 200 (1) + Dimethoxymethane (2)				
$V^E_m/cm^3 \cdot mol^{-1}$	−4.6398	1.4513	−0.6661	1.1132	0.0012
$\Delta\eta/mPa \cdot s$	−72.4612	−36.2065	−10.8831	−1.1416	0.0153
$\Delta R/cm^3 \cdot mol^{-1}$	−16.620	5.3920	−2.0294		0.032
$H^E_m/J \cdot mol^{-1}$	2640.7	−1551.9	980.31	−1898.7	3.1
	PEG 200 (1) + 1,2-Dimethoxyethane (2)				
$V^E_m/cm^3 \cdot mol^{-1}$	−3.8953	1.1802	−0.4028	0.5799	0.0008
$\Delta\eta/mPa \cdot s$	−74.7365	−42.9083	−18.5514	−5.3129	0.00830
$\Delta R/cm^3 \cdot mol^{-1}$	−10.821	2.5930	−0.6593	0.5357	0.003
$H^E_m/J \cdot mol^{-1}$	1530.5	−1128.5	623.35	432.70	2.3
	PEG 400 (1) + Dimethoxymethane (2)				
$V^E_m/cm^3 \cdot mol^{-1}$	−5.0587	3.3679	−2.3929	1.5415	0.0019
$\Delta\eta/mPa \cdot s$	−97.2518	5.2355	12.7990	−5.1447	0.111
$\Delta R/cm^3 \cdot mol^{-1}$	−97.130	57.260	−43.432	31.952	0.14
$H^E_m/J \cdot mol^{-1}$	1932.4	−889.01	1654.7	−2669.3	3.1
	PEG 400 (1) + 1,2-Diethoxyethane (2)				
$V^E_m/cm^3 \cdot mol^{-1}$	−4.2759	3.2375	−1.8381		0.0025
$\Delta\eta/mPa \cdot s$	−108.7779	−16.4667	10.8284	6.5976	0.156
$\Delta R/cm^3 \cdot mol^{-1}$	−83.694	46.294	−30.402	18.853	0.09
$H^E_m/J \cdot mol^{-1}$	1129.6	−622.60	726.17	−994.85	2.9

Table 6. Coefficients of McAllister's Models and Standard Deviations for Kinematic Viscosities at 298.15 K

three-body model			four-body model			
ν_{12}	ν_{21}	$10^6\sigma$ $m^2 \cdot s^{-1}$	ν_{1112}	ν_{1122}	ν_{2221}	$10^6\sigma$ $m^2 \cdot s^{-1}$
PEG 200 (1) + Dimethoxymethane (2)						
14.343	3.357	0.009	17.899	7.471	3.357	0.007
PEG 200 (1) + 1,2-Dimethoxyethane (2)						
12.320	2.808	0.005	16.569	5.973	3.023	0.004
PEG 400 (1) + Dimethoxymethane (2)						
29.037	56.412	0.069	61.167	17.660	62.198	0.017
PEG 400 (1) + 1,2-Dimethoxyethane (2)						
31.108	30.170	0.046	54.025	17.562	34.248	0.011

with mole fraction, was applied to our data. A comparison was performed between the three-body model defined as

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

and the four-body model, given by

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

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.

Conclusions

Trends reported in Figures 1−4 can be interpreted in terms of the molecular interactions of the solution components. The PEGs used in this work are linear chain oligomers, bearing an OH group at each end that can strongly interact via H-bonds. As a consequence, pure PEGs may develop an extended intermolecular cooperative network.[26] Dimethoxymethane and 1,2-dimethoxyethane are linear aliphatic ethers. We performed extended Hückel calculations on these two molecules. Results show that the net charges on the oxygen atoms are nearly the same (−0.85 e) for the two compounds. However, the presence of an additional $-CH_2-$ in 1,2-dimethoxyethane results in quite different properties. The O···O distance in dimethoxymethane is 2.315 Å,[27] whereas in 1,2-dimethoxyethane it has the value 2.884 Å,[28] making the O atoms in this compound more accessible to interactions. Moreover, the extra $-CH_2-$ in 1,2-dimethoxyethane provides a further rotational degree of freedom around the $-CH_2-CH_2-$ bond, so that this molecule is more flexible. Actually, a search in the Cambridge Structural Database (CSD) reports no structure where dimethoxymethane acts as a ligand. In contrast, several hundred structures are reported for 1,2-dimethoxyethane. In fact, 1,2-dimethoxyethane interacts with HO− groups[29] via a normal[30] H-bond (O−H···O distance: 1.965 Å), and it acts also as a bidentate ligand toward metals. This type of interaction leads to a five-membered ring, which is energetically more favored.

Figures 1−3 show that values of V_m^E, $\Delta\eta$, and ΔR are always negative and constantly lower for mixtures with PEG 400, independently of the solvent. These trends can be interpreted as stemming from the weakening and possibly the destruction of the cooperative H-bond structure of PEGs by addition of dimethoxymethane and 1,2-dimethoxyethane molecules. These effects are more evident for PEG 400, since, for the same number of OH end groups, its longer chains reduce the stiffness of the cooperative network of H-bonds. Thus, the interactions developed by solvent molecules are more effective in mixtures with PEG 400 as compared to PEG 200. As regards the solvent role, V_m^E and ΔR data show that deviations are more negative for dimethoxymethane mixtures. This can be attributed to the smaller dimensions of dimethoxymethane molecules, leading to closer packing of the solution components. In contrast, data in Figure 2 show that molecular interactions between components are more important for $\Delta\eta$.

As reported in Figure 4, H_m^E data display positive deviations for all mixtures. The disruption of PEG intermolecular H-bonds upon mixing may account for this behavior. However, values of H_m^E do not follow changes in M_w of the polymers. These trends can be explained by assuming that, at a first approximation, H_m^E is proportional to $E_{11} + E_{22} - 2E_{12}$, where E_{ij} is the interaction energy between molecules i and j. For the mixtures studied in this work E_{22} is clearly the less significant term, since the ether−ether interaction energy is low. For dimethoxymethane solutions also, the E_{12} contribution is small, according to the less effective molecular interactions displayed by this component. In contrast, for 1,2-dimethoxyethane mixtures, the E_{12} term plays a more significant role, mostly for the formation of H-bonds between the OH end groups of PEG and the O atoms of 1,2-dimethoxyethane.

A final observation concerns the position of the minima in Figures 1−3 and of the maximum in Figure 4 with x_1. For PEG 400 solutions they are consistently shifted toward lower values of x_1. This trend is attributable to the larger number of monomeric units at a given molar fraction contained in a molecule of PEG 400 as compared to PEG 200. Thus, the effect of increasing polymer concentration shows up at lower values of x_1 for PEG 400.

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