Molar Heat Capacities, Densities, Viscosities, and Refractive Indices of Poly(ethylene glycols) + 2-Methyltetrahydrofuran at (293.15, 303.15, and 313.15) K

Romolo Francesconi,[†] Adriana Bigi,[†] Katia Rubini,[†] and Fabio Comelli*,[‡]

Dipartimento di Chimica "G. Ciamician", Università degli Studi, via Selmi 2, I-40126 Bologna, Italy, and
Istituto per la Sintesi Organica e la Fotoreattività (ISOF-CNR), via Gobetti 101, I-40129 Bologna, Italy

---

Molar heat capacities, C_p, densities, ρ, dynamic viscosities, η, and refractive indices, n_D, for the binary mixtures poly(ethylene glycol) 200 and poly(ethylene glycol) 400 + 2-methyltetrahydrofuran (MTHF) were determined at (293.15, 303.15, and 313.15) K using a Perkin-Elmer differential scanning calorimeter, an Anton Paar density meter, a Schott-Geräte AVS unit, and an Abbe refractometer, respectively. Excess molar volumes, V_m^E, deviations of the dynamic viscosities, $\Delta\eta$, and deviations of the refractive indices, ΔR, were calculated at these temperatures. These properties were fitted to the Redlich−Kister equation.

Introduction

Poly(ethylene glycols) (PEGs) are a wide group of linear or branched polymers, neutral poly(ethers) of ethylene oxide, which exhibit a wide variety of molecular weights and physical-chemical characteristics. PEGs showing molecular weight, M_w, below 600 are clear, viscous liquids, soluble in most organic solvents, water-soluble, stable, nontoxic compounds that do not hydrolyze or deteriorate on storage. Due to these characteristics, PEGs are used in cosmetics, in foods as additives, in the purifications of biological materials, and in many pharmaceutical properties as cosolvents or vehicles.[1−5]

In this paper, we report experimental data of molar heat capacities, C_p, densities, ρ, dynamic viscosities, η, and refractive indices, n_D, of the binary mixtures containing PEG 200 or PEG 400 + 2-methyltetrahydrofuran (MTHF), respectively. From them, excess molar volumes, V_m^E, deviations of the viscosities, $\Delta\eta$, and deviations of the refractive indices, ΔR, were calculated. The measurements were carried out at atmospheric pressure and at (293.15, 303.15, and 313.15) K. MTHF, a cyclic ether with a CH_3 group close to the O atom, has been chosen for the present study because its properties have been the subject of considerable interest due to the versatility of this compound as a solvent. PEG hydroxyl end groups can interact via strong H-bonds, developing relatively extended networks of associated molecules. Interactions with the ethereal group of the cyclic ether can perturb this H-bond network. Therefore, the thermodynamic and bulk properties of mixtures containing PEGs + MTHF are of interest: the aim of this paper is to determine the extent and type of interactions between these mixtures at two different temperatures in the liquid state. To our knowledge, no data have been reported in the literature on these mixtures.

Experimental Section

Materials. Both PEGs 200 and 400 were Fluka products and were used without further purification. Their average molecular weights (M_n) were determined by gel permeation chromatography (GPC) and were 192 and 365, respectively. 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 that the samples can be considered substantially pure.

MTHF, anhydrous, was from Aldrich showing an analytical grade of +99 % and was used without further purification. Before use, this component was degassed by ultrasound (ultrasonic bath, Hellma, type 460, Milan, Italy) and dried over molecular sieves (Fluka, type 4A) to remove any traces of moisture. The purity of this compound was corroborated by using a Hewlett-Packard G.CX. model 5890 supplied by an HP (cross-linked 5 % ME siloxane) capillary column, and the obtained values complied with purchaser specifications.

Experimental values of densities, viscosities, refractive indices, and heat capacities of the pure liquids are compared with available literature data[6−9] in Table 1.

Heat Capacity Measurements. The heat capacity measurements, C_p, were determined by means of a Perkin-Elmer Pyris Diamond DSC differential scanning calorimeter equipped with a model ULSP 90 intra-cooler. The instrument was calibrated with high-purity standards (indium and cyclohexane) at 5 K·min^{-1}. The temperature was known to within ± 0.1 K. The samples, approximately 10 mg, determined to ± 0.01 mg, were encapsulated in hermetic pans. The heat capacity of the samples was obtained by means of three consecutive DSC runs at a scanning rate of 5 K·min^{-1}: the sample run, the blank run, and the standard sample (sapphire) run.[10] Care was taken to ensure that similar initial and final isotherm levels were reached for all three scans. The heat capacity data were obtained by means of the commercial software supplied by Perkin-Elmer. The estimated relative uncertainty for repeated data is less than 0.1 %.

---

* Corresponding author. E-mail: comelli@isof.cnr.it. Tel: +39-051-2094326. Fax: +39-051-2094325.

[†] Università degli Studi.

[‡] Istituto per la Sintesi Organica e la Fotoreattività (ISOF-CNR).

10.1021/je7003066 CCC: $37.00

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

		ρ/g·cm^{-3}		η/mPa·s		n_D		C_p/J·K^{-1}·mol^{-1}	
component	T/K	this paper	lit.	this paper	lit.	this paper	lit.	this paper	lit.
PEG 200	293.15	1.12480		66.790		1.4626		413.5	
	303.15	1.11698		39.293		1.4582		417.2	
	313.15	1.10898		25.296		1.4547		422.0	
PEG 400	293.15	1.12637		120.752		1.4690		770.0	
	303.15	1.11818		72.066		1.4665		774.5	
	313.15	1.10992		45.977		1.4607		780.7	
MTHF	293.15	0.85295	0.8540[a]	0.492		1.4085	1.40751[a]	155.3	
	303.15	0.84280		0.443		1.4017		158.6	
	313.15	0.83238	0.83365[b]	0.416	0.41[c]	1.3959		162.1	161.56[d]

[a] Ref 6. [b] Ref 7. [c] Ref 8. [d] Ref 9.

Table 2. Experimental Liquid Heat Capacities, C_p^0, of Pure PEG 200 and PEG 400 at Atmospheric Pressure

	C_p^0 (J·mol^{-1}·K^{-1})	
T/K	PEG 200	PEG 400
288.15	412.0	768.6
293.15	413.5	770.0
298.15	416.3	772.8
303.15	417.2	774.5
308.15	419.1	776.7
313.15	422.0	780.7
318.15	424.3	782.5
323.15	426.8	785.1

The experimental heat capacities, C_p^0, of pure components from (288.15 to 323.15) K vs the temperature, at normal pressure, are listed in Table 2 and represented in Figure 1 with the exception of MTHF, whose values are reported in a previous paper.[11] The experimental values of the molar heat capacities, C_p, of mixtures vs the mole fraction, x_1, of PEGs are reported in Table 3 and represented in Figure 2. The expression used to fit C_p^0 as a function of temperature is

$$C_p^0 = c_o + c_1(T/\mathrm{K}) + c_2(T/\mathrm{K})^2 \tag{1}$$

An analogous expression is used to fit C_p as a function of x_1 at any temperature: C_p^0 and (T/K) in eq 1 are substituted by C_p and x_1, respectively.

Values of the parameters c_k are listed in Tables 4 and 5 together with the standard deviations $\sigma(C_p)$.

Density Measurements. Excess molar volumes, V_m^E, with an uncertainty of ± 0.003 cm^3·mol^{-1}, have been determined from density measurements with the help of a digital density meter (Anton Paar, model DMA 60, Graz, Austria) equipped with a measuring cell (Anton Paar, type 602).[12]

All measurements have been determined at a constant temperature using an external ultra-thermostat bath circulator (Heto, type 01 DTB 623, Birkeròd, Denmark), with precision of ± 0.005 K, and temperatures have been detected by a digital thermometer (Anton Paar, type CTK 100). Mixtures were prepared by mass, using a digital balance (Mettler, model AE 160, Switzerland) with an uncertainty of ± 0.0001 g. All masses were corrected for buoyancy and evaporation of components.

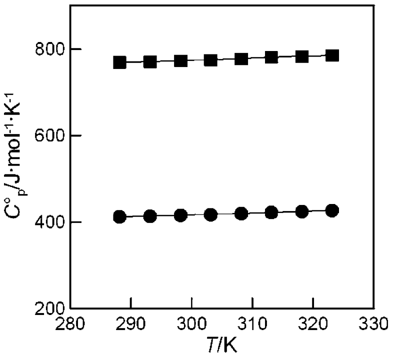

Figure 1. Heat capacities of pure components in the range (288.15 to 333.15) K: full line, eq 1; ●, PEG 200; ■, PEG 400.

Before each series of measurements, the apparatus was calibrated at atmospheric pressure using double-distilled water and dry air, whose densities were taken from the literature.[13,14] The uncertainty in density was ± 1.5·10^{-5} g·cm^{-3} at 308.15 K. Correspondingly, the uncertainty in V_m^E is estimated to be better than ± 0.003 cm^3·mol^{-1}. All molar quantities are based on the IUPAC relative mass atomic table. Before measurements, the apparatus has been checked by determining V_m^E using the test mixture benzene + cyclohexane at 298.15 K. Our results agree with those of the literature[15] showing a discrepancy of ± 0.5 % in the central range of mole fraction of benzene.

The excess molar volumes, V_m^E, 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 components 1 (PEGs) and 2 (MTHF), respectively.

Viscosity Measurements. The kinematic viscosities, ν, were measured with seven Ubbelohde viscosimeters, to cover, with precision, the range of temperatures from (293.15 to 313.15) K. A Schott-Geräte automatic measuring unit (model AVS 350), equipped with a thermostat (Lauda, model E 200, Germany) in which the temperature was regulated to within ± 0.01 K, was used for measurements. An electronic stopwatch was used to measure the flow times. The capillary diameters of the viscosimeters, varying from 0.47 mm to 1.50 mm, were used for kinematic ranges of (0.5 to 30) mm^2·s^{-1}, respectively. The viscosimeters were filled with 15 cm^3 of solution for each measurement. The calibration of the viscosimeters was carried out with double-distilled water and by a standard oil specimen of known viscosity. Experiments were repeated at least five times at each temperature for all mixtures, and the results were averaged. The overall uncertainty of viscosity measurements depends on equilibrium temperature, flow time, mole fraction, and calibration fluid. So, according to the precision of all experimental instruments, the experimental average relative uncertainties of viscosity were estimated to be ± 0.01. The relative uncertainty of the viscosity was about ± 0.02.

The kinematic viscosities ν/cm^2·s^{-1} were obtained from the equation

$$\nu = \eta/\rho = k(t - \theta) \tag{3}$$

Table 3. Experimental Molar Heat Capacities, C_p (Equation 1), for Binary Mixtures Containing PEGs + MTHF

PEG 200 (1) + MTHF (2)

x_1	C_p/J·mol^{-1}·K^{-1}	x_1	C_p/J·mol^{-1}·K^{-1}	x_1	C_p/J·mol^{-1}·K^{-1}	x_1	C_p/J·mol^{-1}·K^{-1}
			T/K = 293.15				
0.0651	172.6	0.2198	214.3	0.5151	292.2	0.8331	373.0
0.1140	185.7	0.3677	253.7	0.6045	315.2	0.9005	389.6
0.1922	206.9	0.4736	281.5	0.6898	337.0	0.9370	398.5
			T/K = 303.15				
0.0651	176.2	0.2198	218.0	0.5151	296.3	0.8331	377.0
0.1140	189.4	0.3677	257.6	0.6045	319.4	0.9005	393.4
0.1922	210.6	0.4736	285.5	0.6898	341.1	0.9370	402.3
			T/K = 313.15				
0.0651	179.7	0.2198	221.5	0.5151	300.0	0.8331	380.1
0.1140	193.0	0.3677	261.1	0.6045	323.0	0.9005	396.8
0.1922	214.1	0.4736	289.2	0.6898	344.5	0.9370	405.9

PEG 400 (1) + MTHF (2)

x_1	C_p/J·mol^{-1}·K^{-1}	x_1	C_p/J·mol^{-1}·K^{-1}	x_1	C_p/J·mol^{-1}·K^{-1}	x_1	C_p/J·mol^{-1}·K^{-1}
			T/K = 293.15				
0.0454	183.9	0.1849	267.9	0.5086	464.6	0.7631	621.7
0.1011	217.4	0.2926	333.0	0.6289	538.7	0.8804	694.3
0.1424	242.0	0.3980	397.3	0.6774	568.7	0.8998	706.4
			T/K = 303.15				
0.0454	187.2	0.1849	272.1	0.5086	469.8	0.7631	626.7
0.1011	221.0	0.2926	337.7	0.6289	543.8	0.8804	699.1
0.1424	246.1	0.3980	402.0	0.6774	573.8	0.8998	711.2
			T/K = 313.15				
0.0454	191.3	0.1849	277.9	0.5086	477.0	0.7631	634.0
0.1011	225.7	0.2926	344.3	0.6289	551.2	0.8804	706.0
0.1424	251.3	0.3980	409.0	0.6774	581.1	0.8998	718.1

where η is the absolute (dynamic) viscosity; ρ is the density; k/cm^2·s^{-1} is the capillary constant; t is the flow time; and θ is the kinetic energy correction. In the whole set of experiments, flow times were maintained >200 s, by selecting viscosimeters with appropriate values of k.

Equation 3 and the values of ρ allow calculation of the deviation in viscosity, $\Delta\eta$, from the definition

$$\Delta\eta = \eta - \omega_1\eta_1 - \omega_2\eta_2 \tag{4}$$

where η_k is the viscosity of the pure component k and ω_k is its mass fraction in the mixture.

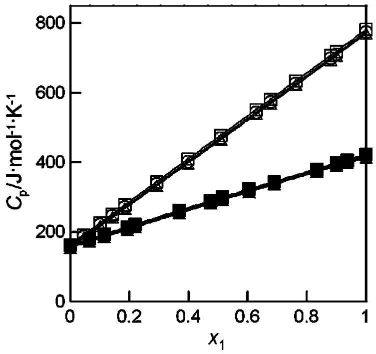

Figure 2. Molar heat capacities, C_p, for the binary mixtures PEG 200 (1) + MTHF (2) (full points) and PEG 400 (1) + MTHF (2) (open points): ▲,△, T/K = 293.15; ●,○, T/K = 303.15; ■,□, T/K = 313.15; full line, eq 1.

Table 4. Adjustable Parameters of Equation 1 and Standard Deviation of Pure Components

component	c_0	c_1	c_2	$\sigma(C_p)$/J·mol^{-1}·K^1
PEG 200	579.1381	−1.4716	0.0031	0.45
PEG 400	829.2998	−1.2465	0.0028	0.55

Table 5. Adjustable Parameters of Equation 1 and Standard Deviation of PEGs (1) + MTHF (2) at (293.15, 303.15, and 313.15) K

T/K	c_0	c_1	c_2	$\sigma(C_p)$/J·mol^{-1}·K^{-1}
		PEG 200 (1) + THP (2)		
293.15	154.8450	274.7203	−15.7257	0.22
303.15	158.1908	277.2510	−17.8938	0.23
313.15	161.8267	276.2274	−16.5661	0.29
		PEG 400 (1) + MTHF (2)		
293.15	156.2257	600.0596	13.0846	0.42
303.15	159.4097	606.2397	8.1864	0.39
313.15	163.0381	618.4728	-1.5044	0.46

Refractive Indices Measurements. Refractive indices at the sodium D-line, n_D, were determined using a thermostated Abbe refractometer (Carl Zeiss, model G, Jena, Switzerland) with an accuracy 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. Calibration was performed by measuring the refractive indices of doubly distilled water, toluene, cyclohexane, and carbon tetrachloride at defined temperatures.[6] 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.

The solutions were pre-thermostated at the three temperatures before the experiments to achieve a quick thermal equilibrium.

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

$$\Delta R = R_m - \sum_{i=1}^{2} R_i\varphi_i \tag{5}$$

with R_i and R_m being the molar refraction of pure components and of the mixture, respectively, and φ_i being the volume

Table 6. Densities, ρ, Excess Molar Volumes, V_m^E, Dynamic Viscosities, η, Deviations in Dynamic Viscosities, $\Delta\eta$, Refracive Indices, n_D, and Deviations in Refractive Indices, ΔR, of PEGs + MTHF at (293.15, 303.15, and 313.15) K

PEG 200 (1) + MTHF (2)

x_1	ρ $\mathrm{g \cdot cm^{-3}}$	V_m^E $\mathrm{cm^3 \cdot mol^{-1}}$	η mPa·s	$\Delta\eta$ mPa·s	n_D	ΔR $\mathrm{cm^3 \cdot mol^{-1}}$	x_1	ρ $\mathrm{g \cdot cm^{-3}}$	V_m^E $\mathrm{cm^3 \cdot mol^{-1}}$	η mPa·s	$\Delta\eta$ mPa·s	n_D	ΔR $\mathrm{cm^3 \cdot mol^{-1}}$
						T/K = 293.15							
0.0457	0.87427	−0.122	0.635	−2.885	1.4131	−0.639	0.5284	1.03424	−0.452	9.283	−26.242	1.4463	−2.710
0.1033	0.89925	−0.243	0.894	−6.449	1.4185	−1.302	0.6311	1.05783	−0.395	14.926	−27.409	1.4506	−2.416
0.1593	0.92149	−0.322	1.255	−9.795	1.4231	−1.819	0.7485	1.08182	−0.299	24.826	−25.289	1.4550	−1.850
0.2576	0.95687	−0.428	2.246	−15.326	1.4305	−2.441	0.8597	1.10214	−0.186	38.967	−18.522	1.4588	−1.116
0.3636	0.99027	−0.482	4.044	−20.557	1.4374	−2.771	0.9234	1.11279	−0.105	50.671	−11.042	1.4607	−0.628
0.4484	1.01392	−0.477	6.248	−23.969	1.4424	−2.804	0.9633	1.11916	−0.051	58.558	−5.802	1.4616	−0.318
						T/K = 303.15							
0.0804	0.87971	−0.215	0.697	−2.871	1.4102	−1.029	0.6879	1.06185	−0.440	13.010	−14.160	1.4483	−2.137
0.1348	0.90247	−0.337	0.932	−4.751	1.4154	−1.564	0.7496	1.07416	−0.375	16.536	−13.031	1.4508	−1.799
0.2233	0.93587	−0.465	1.520	−7.616	1.4225	−2.219	0.7987	1.08341	−0.315	19.857	−11.616	1.4524	−1.512
0.3741	0.98473	−0.585	3.308	−11.668	1.4327	−2.759	0.8664	1.09540	−0.215	25.232	−8.871	1.4547	−1.041
0.5026	1.01972	−0.578	5.993	−13.977	1.4401	−2.731	0.9253	1.10522	−0.120	30.820	−5.570	1.4562	−0.616
0.5842	1.03941	−0.545	8.519	−14.620	1.4440	−2.546	0.9643	1.11146	−0.060	35.081	−2.823	1.4576	−0.273
						T/K = 313.15							
0.0425	0.85266	−0.143	0.497	−0.977	1.4014	−0.538	0.5219	1.01590	−0.657	4.986	−8.416	1.4373	−2.649
0.1003	0.87821	−0.294	0.674	−2.238	1.4072	−1.199	0.6386	1.04305	−0.563	7.763	−8.543	1.4430	−2.288
0.1612	0.90311	−0.438	0.928	−3.498	1.424	−1.775	0.7479	1.06565	−0.446	11.469	−7.555	1.4473	−1.772
0.2267	0.92759	−0.540	1.306	−4.749	1.4182	−2.194	0.8620	1.08659	−0.265	16.813	−5.060	1.4510	−1.057
0.3259	0.96106	−0.655	2.122	−6.402	1.4260	−2.574	0.9248	1.09707	−0.141	20.280	−3.144	1.4527	−0.608
0.4440	0.99564	−0.681	3.604	−7.860	1.4329	−2.745	0.9601	1.10276	−0.073	22.626	−1.679	1.4534	−0.352

PEG 400 (1) + MTHF (2)

x_1	ρ $\mathrm{g \cdot cm^{-3}}$	V_m^E $\mathrm{cm^3 \cdot mol^{-1}}$	η mPa·s	$\Delta\eta$ mPa·s	n_D	ΔR $\mathrm{cm^3 \cdot mol^{-1}}$	x_1	ρ $\mathrm{g \cdot cm^{-3}}$	V_m^E $\mathrm{cm^3 \cdot mol^{-1}}$	η mPa·s	$\Delta\eta$ mPa·s	n_D	ΔR $\mathrm{cm^3 \cdot mol^{-1}}$
						T/K = 293.15							
0.0567	0.89897	−0.226	0.985	−6.328	1.4194	−6.823	0.5230	1.06830	−0.495	27.459	−35.935	1.4573	−16.616
0.0933	0.92327	−0.323	1.488	−10.222	1.4252	−10.069	0.6664	1.09106	−0.364	48.341	−32.287	1.4619	−12.918
0.1311	0.94510	−0.406	2.213	−14.046	1.4303	−12.682	0.7522	1.10206	−0.281	63.037	−27.911	1.4635	−10.147
0.2052	0.98040	−0.534	4.261	−20.906	1.4383	−16.116	0.7869	1.10607	−0.243	70.055	−25.074	1.4649	−8.800
0.2970	1.01387	−0.587	8.237	−27.973	1.4456	−18.115	0.8709	1.11489	−0.156	88.408	−16.819	1.4667	−5.526
0.4164	1.04630	−0.565	16.509	−34.056	1.4528	−18.164	0.9111	1.11872	−0.114	98.734	−11.329	1.4676	−3.844
						T/K = 303.15							
0.0535	0.88676	−0.242	0.828	−3.446	1.4130	−6.485	0.4686	1.04906	−0.603	14.746	−19.257	1.4502	−17.729
0.0930	0.91358	−0.386	1.264	−5.841	1.4195	−10.046	0.5848	1.07039	−0.502	23.227	−19.100	1.4548	−15.404
0.1296	0.93493	−0.478	1.801	−7.924	1.4253	−12.552	0.6790	1.08444	−0.415	31.876	−17.200	1.4579	−12.719
0.1780	0.95927	−0.575	2.729	−10.466	1.4275	−15.052	0.7549	1.09413	−0.338	40.448	−14.063	1.4595	−10.239
0.2332	0.98244	−0.621	4.066	−13.083	1.4353	−17.025	0.8664	1.10628	−0.210	54.034	−8.463	1.4623	−5.970
0.3324	1.01562	−0.657	7.562	−16.690	1.4428	−18.490	0.9337	1.11261	−0.116	62.937	−4.381	1.4636	−3.1800
						T/K = 313.15							
0.0551	0.87812	−0.3128	0.759	−2.166	1.4076	−6.580	0.4818	1.04345	−0.7541	11.308	−11.060	1.4476	−17.243
0.0896	0.90189	−0.4606	1.056	−3.444	1.4139	−9.645	0.5963	1.06400	−0.6311	16.959	−10.625	1.4515	−14.776
0.128	0.92471	−0.5799	1.491	−4.757	1.4197	−12.321	0.6603	1.07360	−0.5527	20.688	−9.810	1.4531	−13.021
0.2015	0.96053	−0.7154	2.646	−6.951	1.4281	−15.805	0.7485	1.08511	−0.4319	26.256	−8.263	1.4558	−10.101
0.3022	0.99781	−0.8039	4.929	−9.257	1.4371	−17.945	0.867	1.09804	−0.243	35.445	−4.474	1.4585	−5.616
0.3811	1.02041	−0.8062	7.361	−10.420	1.4418	−18.222	0.9358	1.10447	−0.1176	40.368	−2.684	1.4597	−2.781

fraction of the ith component, given as

$$\varphi_i = x_i V_i / \sum_{i=1}^{2} x_i V_i \tag{6}$$

where $V_i = M_i/\rho_i$.

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

$$R_i = \{[n^2_{D(i)} - 1]/[n^2_{D(i)} + 2]\} \cdot V_i \tag{7}$$

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

Results and Discussion

Table 6 collects densities, ρ, excess molar volumes, V_m^E, dynamic viscosities, η, deviations in viscosities, $\Delta\eta$, refractive indices, n_D, and deviations in refractive indices, ΔR. These values are also graphically represented in Figures 3 to 5.

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

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

where Q refers to V_m^E, $\Delta\eta$, and ΔR.

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 7. The standard deviations, $\sigma(Q)$, reported in Table 7 were defined as

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

Table 7. Adjustable Parameters, a_k, from Equation 8, and Standard Deviations, $\sigma(Q)$, from Equation 9, of PEGs + MTHF at (293.15, 303.15, and 313.15) K

function	T/K	a_0	a_1	a_2	a_3	$\sigma(Q)$
		PEG 200 (1) + MTHF (2)				
V^E_m/cm^3·mol^{-1}	293.15	−1.8559	0.6768	−0.2952		0.004
	303.15	−2.3325	0.6710			0.004
	313.15	−2.6879	0.7464			0.007
$\Delta\eta$/mPa·s	293.15	−102.4096	−54.8644	−17.3901		0.18
	303.15	−55.8327	−24.6184	−5.1539		0.02
	313.15	−33.5693	−12.2100			0.07
ΔR/cm^3·mol^{-1}	293.15	−11.0667	3.0636	−0.8705		0.01
	303.15	−11.0622	2.9857			0.02
	313.15	−67.4339	34.7219	−21.7717	12.7907	0.07
		PEG 400 (1) + MTHF (2)				
V^E_m/cm^3·mol^{-1}	293.15	−2.0511	1.5168	−0.8530		0.005
	303.15	−2.2955	1.6059	−1.3395		0.005
	313.15	−2.9184	1.6846	−1.2655	0.7237	0.007
$\Delta\eta$/mPa·s	293.15	−143.1299	−16.6263	13.9676		0.29
	303.15	−78.0661	−2.9023	11.3388		0.14
	313.15	−44.3708	0.5904	4.2554		0.15
ΔR/cm^3·mol^{-1}	293.15	−68.0009	35.0829	−22.5552	13.3099	0.05
	303.15	−68.5737	34.9351	−23.6580	10.0011	0.09
	313.15	−10.8185	2.9216			0.02

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

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

where $\epsilon_k = Q_{\text{calcd}} - Q$. Q is the experimental value, and Q_{calcd} is evaluated through eq 8.

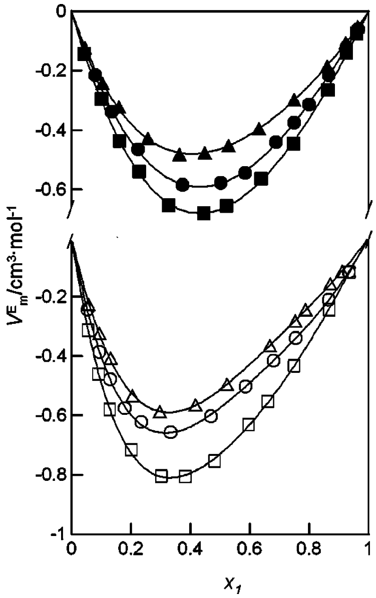

Figure 3. Excess molar volumes, V^E_m, for the binary mixtures PEG 200 (1) + MTHP (2) (full points), and PEG 400 (1) + MTHF (2) (open points): ▲,△, T/K = 293.15; ●,○, T/K = 303.15; ■,□, T/K = 313.15; full line, eq 8.

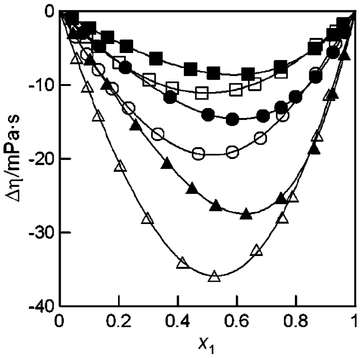

Figure 4. Experimental deviation in viscosities, $\Delta\eta$, for the binary mixtures PEG 200 (1) + MTHF (2) (full points) and PEG 400 (1) + MTHF (2) (open points): ▲,△, T/K = 293.15; ●,○, T/K = 303.15; ■,□, T/K = 313.15; full line, eq 8.

Values of V^E_m are always negative, the PEG 400 + MTHF mixture showing more negative V^E_m values than those of PEG 200. Both PEGs give the same temperature dependence of V^E_m, that is, a decrease of V^E_m with an increase of temperature.

Similar results were obtained in a previous paper[16] for the same PEGs in a mixture with THF(oxolane).

However, comparison of V^E_m at the same temperature of 303.15 K leads to values of V^E_m that are almost doubled when the solvent is MTHF (present paper).

As pointed out in a previous paper,[16] mixing of PEG with monoethers leads to partial disruption of the cooperative H-bond configuration of PEG through the interactions of ether with polymers. The presence of a CH_3 group in MTHF may explain the different behavior of MTHF with respect to THF because interactions between PEGs and MTHF will be enhanced by the CH_3 group which induces larger negative charge to the O atoms of cyclic ether. Moreover, positively charged CH_3 can interact with the large number of O atoms of PEGs, which explains the more negative V^E_m when passing from PEG 200 to PEG 400.

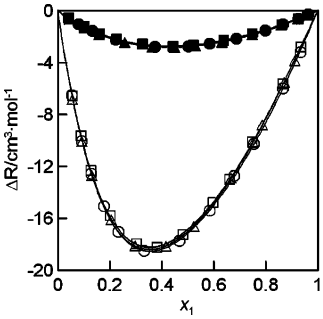

Figure 5. Deviation in refractive indices, ΔR, for the binary mixtures PEG 200 (1) + MTHF (2) (full points) and PEG 400 (1) + MTHF (2) (open points): ▲,△, T/K = 293.15; ●,○, T/K = 303.15; ■,□, T/K = 313.15; full line, eq 5.

Also, the effect of temperature on $V_{\mathrm{m}}^{\mathrm{E}}$ is clear, if we consider the larger disruption of the PEG configurations with the increasing temperature.

The viscosity data may be interpreted analogously because disruption of configurations and volume reduction after mixing are consistent with smaller values of η.

As for the calorimetric data, both C_p^0 and C_p show a linear dependence on temperature and composition, respectively.

Literature Cited

(1) Harris, J. M. *Poly(ethylene glycol) Chemistry, Biothecnical and Biomedical Application;* Plenum Press: New York, 1992.

(2) Powell, G. M. Polyethylene Glycol. In *Handbook of water-soluble gums and resins;* Davidson, R. L., Ed.; McGraw-Hill Book Company: New York, 1980; Chapter 18.

(3) Coimbra, J. S. R.; Mojola, F.; Mereilles, A. J. A. Dispersed phase hod up in a perforated rotating disc contractor (PRDC) using aqueous two-phase systems. *J. Chem. Eng. Jpn.* **1998**, *31*, 277−280.

(4) Ninni, L. H.; Camargo, M. S.; Mereilles, A. J. A. Water activity in poly(ethylene glycol) aqueous solutions. *Thermochim. Acta* **1999**, *328*, 169−176.

(5) Comelli, F.; Ottani, S.; Francesconi, R.; Castellari, C. 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. *J. Chem. Eng. Data* **2002**, *47*, 1226−1231.

(6) Riddick, J. A.; Bunger, W. B.; Sakano, T. K.; *Organic Solvents*, 4th ed.; Wiley-Interscience: New York, 1986.

(7) De Lorenzi, L.; Fermeglia, M.; Torriano, G. Density and Viscosity of 1-Methoxy-2-propanol, 2-Methyltetrahydrofuran, α,α,α-Trifluoroethane, and Their Binary Mixtures with 111-Trichloroethane at Different Temperatures. *J. Chem. Eng. Data* **1996**, *41*, 1121−1125.

(8) Giner, B.; Aldea, M.; Mertin, S.; Gascon, I.; Lafuente, C. Viscosities of Binary Mixtures of Isomeric Butanols or Isomeric Chlorobutanes with 2-Methyltetyrahydrofuran. *J. Chem. Eng. Data* **2003**, *48*, 1296−1300.

(9) Rodriguez, S.; Lafuente, C.; Artigas, H.; Royo, F. M.; Urieta, J. S. Densities, Speeds of Sound, and Isentropic Compressibilities of a Cyclic Ether with Chlorocyclohexane, or Bromocyclohexane at the Temperature 298.15 K and 313.15 K. *J. Chem. Thermodyn.* **1999**, *31*, 139−149.

(10) O'Neill, M. J. Measurement of specific heat functions by differential scanning calorimetry. *Anal. Chem.* **1966**, *38*,1331.

(11) Comelli, F.; Francesconi, R.; Bigi, A.; Rubini, K. Molar Heat Capacities, Densities, Viscosities, and Refractive Indices of Dimethyl Sulfoxide + Tetrahydropyran and + 2-Methyltetrahydrofuran at (293.15, 303.15, and 313.15) K. *J. Chem. Eng. Data* **2007**, *52*, 639−644.

(12) Fermeglia, M.; Lapasin, J. Excess Volumes and Viscosities of Binary Mixtures of Organics. *J. Chem. Eng. Data* **1988**, *33*, 415−417.

(13) Kohlrausch, F. Density of Air. *Prakt. Phys.* **1968**, *3*, 40.

(14) Wagenbreth, H.; Blanke, W. Die Dichte des Wassers im Internationalen Einheitensystem und in die Internationalen Practishen Temperaturskala von 1968. PTB − Mitteilungen. 1971; Vol. 6/71, p 412.

(15) Wilhelm, E. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1985**, 164.

(16) Ottani, S.; Vitalini, D.; Comelli, F.; Castellari, C. Densities, Viscosities, and Refractive Indices of Poly(ethylene glycol) 200 and 400 + Cyclic Ethers at 303.15 K. *J. Chem. Eng. Data* **2002**, *47*, 1197−1204.

Received for review May 31, 2007. Accepted July 11, 2007.

JE7003066