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Densities, Viscosities, Refractive Indices, and Heat Capacities of Four Poly(ethylene glycol)−Poly(propylene glycol)−Poly(ethylene glycol)-*block*-Copolymers + Dimethyl Sulfoxide at (298.15 and 313.15) K and at Atmospheric Pressure

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Densities, ρ, dynamic viscosities, η, refractive indices, n_D, and heat capacities, C_p, for the binary mixtures containing four *block*-copolymers [poly(ethylene glycol)−poly(propylene glycol)−poly(ethylene glycol)] ($M_n = 1100$, $M_n = 1900$, $M_n = 2000$, and $M_n = 2800$) + dimethyl sulfoxide were determined at (298.15 and 313.15) K and at atmospheric pressure using an Anton Paar density meter, a Schott-Geräte AVS viscometer, an Abbe refractometer, and a Perkin-Elmer differential scanning calorimeter. Volume variations, ΔV, during mixing and deviations of the dynamic viscosities, $\Delta\eta$, were obtained at these temperatures and are negative for all mixtures. Experimental data were fitted to the Redlich−Kister equation, and the adjustable parameters and the standard deviations between experimental and calculated values were estimated.

Introduction

In a previous article,[1] we reported experimental thermodynamic and bulk properties for binary mixtures containing two *block*-[poly(ethylene glycol)−poly(propylene glycol)−poly(ethylene glycol)]copolymers (COP) + 2-methyltetrahydrofuran. The present article continues this work, reporting values of densities, ρ, dynamic viscosities, η, refractive indices, n_D, and heat capacities, C_p, of binary mixtures containing four *block*-copolymers (COP) (molecular weights varying from 1100 to 2800) + dimethyl sulfoxide (DMSO) at (298.15 and 313.15) K and at normal pressure. COPs are amphiphilic copolymers, which have been extensively studied as potential drug delivery vehicles because of their excellent biocompatibility and environmental friendly behavior.[2] These copolymers are commercially available (under the name of “pluronic” or “poloxamer”) and are widely applied as emulsifiers, wetting agents, solubilizers, and so on.[3] DMSO was chosen because of its wide range of applicability as a solvent in chemical and biological processes, pharmaceutical applications, veterinary medicine, and microbiology.[4−6] DMSO exhibits strong self-association. It is a highly polar aprotic solvent because of its S=O group, and it has a large dipole moment and relative permittivity, showing values of $\mu = 4.06$ D and $\varepsilon = 46.45$ at 298.15 K. The thermodynamic properties of DMSO + COPs depend on the interactions between the S=O group of DMSO and the −OH groups of the copolymers. This article aims to determine these properties with the purpose of obtaining some insight into interactions between molecules.

No data on the binary mixtures studied in this article have been found in the literature.

Experimental Section

Materials. All products were from Aldrich and were used as received. The *Block*-copolymers show molecular weights M_n $=1100$, $M_n = 1900$, $M_n = 2000$, and $M_n = 2800$ and are named COP1, COP2, COP3, and COP4, respectively. DMSO (anhydrous, analytical grade 99.7 %) was degassed by ultrasound (ultrasonic bath, Hellma, type 460, Milan, Italy) before use and dried over molecular sieves (Fluka, type 4Å) to remove any traces of moisture. The purity of this compound was corroborated by the use of a Hewlett-Packard G.CX. model 5890 apparatus supplied by an HP (cross-linked 5 % ME siloxane) capillary column, and the obtained values complied with purchaser specifications. Experimental values of densities, ρ, dynamic viscosities, η, refractive indices, n_D, and heat capacities, C_p, of the pure liquids are compared with available literature data[1,7−10] in Table 1. COP1 and COP2 are the same products as those used in the previous article,[1] but because they come from different lots, they show some differences in their properties. The new values of physical constants for these compounds are also reported in Table 1.

Characterization of Copolymers. Samples used in this work are *block* copolymers having the following general structure

$$\mathrm{HO{-}({-}CH_2{-}CH_2{-}O{-})_{\mathit{n}}{-}[{-}CH(CH_3){-}CH_2{-}O{-}]_{\mathit{m}}{-}({-}CH_2{-}CH_2{-}O{-})_{\mathit{p}}{-}H}$$

The relative abundance of ethylene glycol (EG, $-CH_2-CH_2-O-$) and propylene glycol (PG, $-CH(CH_3)-CH_2-O-$) units in each copolymer sample has been achieved by ^{1}H NMR analysis. In the spectra of all samples (omitted for brevity), two clusters of signals are present between (1.0 and 1.2) ppm (due to the CH_3 group of PG) and between (3.3 and 3.8) ppm (due to CH_2 groups

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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·g^{-1}·K^{-1}	
	T/K	this article	lit.	this article	lit.	this article	lit.	this article	lit.
COP1	298.15	1.01899	1.01856[a]	169.721	170.295[a]	1.4534	1.4533[a]	1.89441	1.89442[a]
	313.15	1.00660	1.00667[a]	78.892	79.396[a]	1.4473	1.4470[a]	1.93586	1.93581[a]
COP2	298.15	1.05758	1.05747[a]	361.197	360.679[a]	1.4611	1.4608[a]	2.02554	2.02783[a]
	313.15	1.04504	1.04567[a]	172.435	174.291[a]	1.4550	1.4549[a]	2.09214	2.09600[a]
COP3	298.15	1.01738		324.284		1.4540		1.90749	
	313.15	1.00522		149.264		1.4475		1.95619	
COP4	298.15	1.02065		500.392		1.4552		1.91034	
	313.15	1.00828		234.263		1.4494		1.93652	
DMSO	298.15	1.09532	1.09537[b]	2.0006	1.991[b]	1.4778	1.4775[b]	1.93333	1.91207[c]
	298.15								1.95162[d]
	313.15	1.07983	1.08043[e]	1.52530	1.5126[e]	1.4707	1.4707[e]	1.96027	

[a] ref 1. [b] ref 7. [c] ref 8 (converted in J·g^{-1}·K^{-1}). [d] ref 9 (converted in J·g^{-1}·K^{-1}). [e] ref 10.

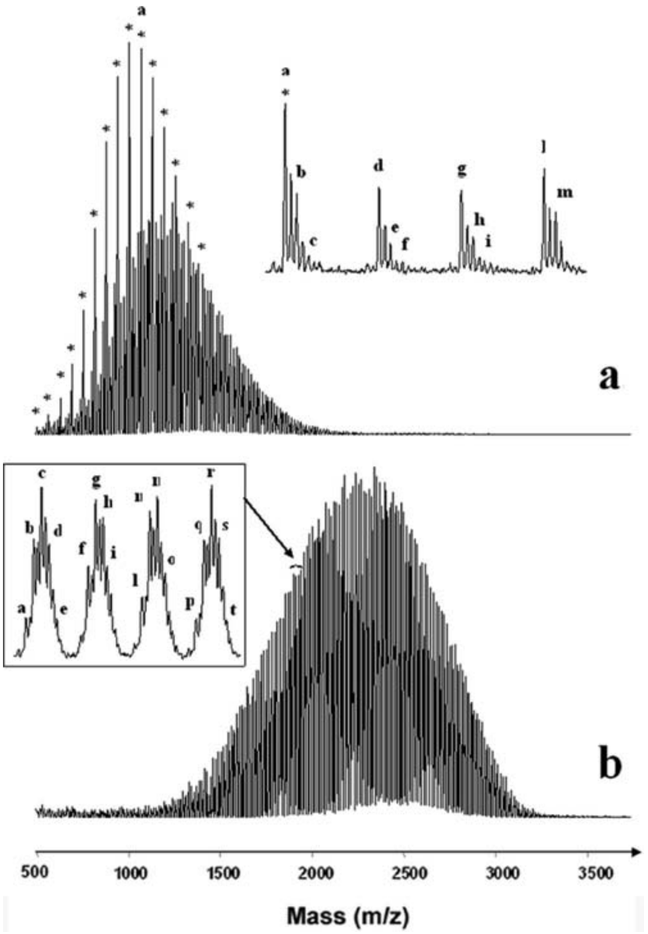

Figure 1. Positive MALDI-TOF mass spectrum of (a) COP1 and (b) COP2. In the spectrum of COP1, peaks due to omopolypropylene glycol are indicated with $*$. In the insets, for each peak due to an oligomeric species present in the copolymer, the *m/z* value and, in parenthesis, the number of ethylene glycol (EG) and propylene glycol (PG) units constituting the molecule are indicated. Inset of a: (a) *m/z* 1027 (0, 15), (b) *m/z* 1029 (4, 14), (c) *m/z* 1031 (8, 11), (d) *m/z* 1043 (3, 15), (e) *m/z* 1045 (7, 12), (f) *m/z* 1047 (11, 9), (g) *m/z* 1057 (2, 16), (h) *m/z* 1059 (6, 13), (i) *m/z* 1061 (10, 10), (l) *m/z* 1071 (1, 17), (m) *m/z* 1073 (5, 14). Inset of b: (a) *m/z* 1905 (16, 20), (b) *m/z* 1907 (20, 17), (c) *m/z* 1909 (24, 14), (d) *m/z* 1911 (28, 11), (e) *m/z* 1913 (32, 8), (f) *m/z* 1921 (19, 18), (g) *m/z* 1923 (23, 15), (h) *m/z* 1925 (27, 12), (i) *m/z* 1927 (31, 9), (l) *m/z* 1935 (18, 19), (m) *m/z* 1937 (22, 16), (n) *m/z* 1939 (26, 13), (o) *m/z* 1941 (30, 10), (p) *m/z* 1949(17, 20), (q) *m/z* 1951 (21, 17), (r) *m/z* 1953 (25, 14), (s) *m/z* 1955 (29, 11), (t) *m/z* 1957 (33, 8).

of PG and EG and to the CH group of PG). On the basis of the intensities of these signals, the values of $[n + p]$ (% mol EG component abundance) and $[m]$ (% mol PG component abundance) have been determined. The results obtained, in accordance with those indicated by the supplier, are reported in Table 2.

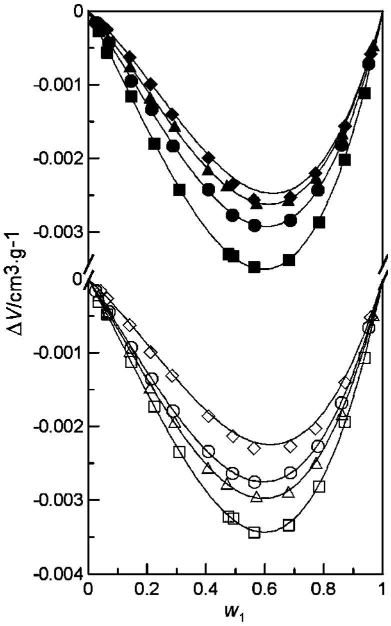

Figure 2. Volume variations, ΔV, for the binary mixtures containing *block*-copolymers (1) + DMSO (2): (●,○), COP1 + DMSO; (■,□), COP2 + DMSO; (▲,△), COP3 + DMSO; (◆,◇), COP4 + DMSO. Open points, T/K = 298.15; full points, T/K = 313.15; full lines, eq 5.

The characterization of copolymer samples, to determine both average molecular weight and microstructure, has been attempted by MALDI-TOF mass spectrometry.[1]

In Figure 1, as an example, the mass spectra of COP1 (Figure 1a) and COP2 (Figure 1b) are reported. In the spectrum of COP1, a series of peaks (indicated with $*$) at *m/z* $(18 + 23) + x \cdot 58$ (of which the first member, with $x = 9$, is present at *m/z* 563) corresponding to homopropylene glycol oligomers cationized by Na$^+$ is present with an intensity higher than the expected. A similar behavior is found also in the spectrum of COP3, whereas in the spectra of COP2 (Figure 1b) and COP4, this anomalous distribution is absent.

Although each signal of the overall mass spectra reported in Figure 1 looks like a single peak, it is really constituted of a cluster of peaks due not only to the isotopic pattern of the different compounds but also mostly to the presence of oligomers of different composition. This fact is well evidenced in the insets of Figure 1a,b (enlargement of the zone of the spectrum included between *m/z* 1025 and 1075 and *m/z* 1900 and 1960, respectively) in which, on the top of each peak due

Table 2. Chemical Composition and Average Molecular Weight of the Polymers Used

sample	EG wt % (Aldrich)	PG wt % (Aldrich)	EG mol % (wt %) (our data)	PG mol % (wt %) (our data)	M_n (Aldrich)	M_n (our data)	M_w (our data)	M_w/M_n (our data)
COP1	15[a]	85[a]	19 (15)	81 (85)	~ 1100	1237	1289	1.042
COP1*[c]	13[a]	87[a]	19	81	~ 1100	1220	1320	1.08
COP2	50[a]	50[a]	58 (51)	42 (49)	~ 1900	2109	2207	1.046
COP2*[c]	57[a]	43[a]	59	41	~ 1900	2280	2510	1.10
COP3	14.5[a]	85.5[a]	18 (14)	82 (86)	~ 2000	2000	2102	1.050
COP4	10[b]	90[b]	20 (16)	80 (84)	~ 2800	2716	2888	1.063

[a] Data concerning the specific lot used. [b] Nominal content of EG and PG in the copolymer. [c] Data concerning copolymers analyzed in a previous work.[1]

Table 3. Densities, ρ, Volume Variations, ΔV, Dynamic Viscosities, η, Deviations in Dynamic Viscosities, $\Delta\eta$, Refractive Indices, n_D, of *block*-Copolymers (COP) + DMSO at (298.15 and 313.15) K

w_1	ρ $g\cdot cm^{-3}$	ΔV $cm^3\cdot g^{-1}$	η mPa·s	$\Delta\eta$ mPa·s	n_D	w_1	ρ $g\cdot cm^{-3}$	ΔV $cm^3\cdot g^{-1}$	η mPa·s	$\Delta\eta$ mPa·s	n_D
		COP1 (1) + DMSO (2)						COP3 (1) + DMSO (2)			
		T/K = 298.15						T/K = 298.15			
0.0248	1.09340	−0.00016	2.233	−3.93	1.4774	0.0347	1.09268	−0.00022	2.400	−10.795	1.4774
0.0701	1.09006	−0.00044	2.666	−11.091	1.4765	0.0671	1.09026	−0.00045	2.819	−20.822	1.4766
0.1459	1.08452	−0.00093	3.642	−22.827	1.4752	0.1427	1.08463	−0.00098	4.210	−43.772	1.4752
0.2142	1.07954	−0.00135	4.882	−33.037	1.4736	0.2102	1.07968	−0.00147	6.080	−63.659	1.4737
0.2884	1.07417	−0.00179	6.735	−43.627	1.4718	0.2927	1.07354	−0.00194	9.339	−86.990	1.4719
0.4071	1.06552	−0.00234	11.437	−58.844	1.4690	0.4061	1.06518	−0.00256	16.749	−116.116	1.4693
0.4902	1.05945	−0.00264	16.401	−67.820	1.4669	0.4710	1.06030	−0.00278	23.182	−130.599	1.4677
0.5644	1.05392	−0.00276	23.031	−73.638	1.4650	0.5717	1.05262	−0.00295	38.621	−147.622	1.4652
0.6861	1.04462	−0.00263	40.354	−76.726	1.4617	0.6791	1.04429	−0.00289	66.124	−154.751	1.4623
0.7805	1.03724	−0.00227	63.444	−69.470	1.4594	0.7731	1.03675	−0.00249	106.629	−144.537	1.4603
0.8595	1.03084	−0.00168	91.882	−54.271	1.4572	0.8617	1.02943	−0.00183	166.613	−113.101	1.4577
0.9534	1.02300	−0.00066	140.039	−21.865	1.4543	0.9684	1.02019	−0.00049	280.867	−33.219	1.4546
		T/K = 313.15						T/K = 313.15			
0.0248	1.07794	−0.00015	1.670	−1.775	1.4702	0.0347	1.07723	−0.00015	1.805	−4.852	1.4703
0.0701	1.07473	−0.00043	1.986	−4.962	1.4696	0.0671	1.07493	−0.00039	2.112	−9.334	1.4696
0.1459	1.06947	−0.00095	2.689	−10.123	1.4679	0.1427	1.06937	−0.00075	3.804	−19.520	1.4681
0.2142	1.06468	−0.00133	3.457	−14.637	1.4664	0.2102	1.06456	−0.00117	4.254	−28.324	1.4667
0.2883	1.05961	−0.00183	4.623	−19.211	1.4648	0.2927	1.05861	−0.00156	6.316	−38.451	1.4649
0.4071	1.05137	−0.00242	7.399	−25.624	1.4620	0.4061	1.05061	−0.00215	10.750	−50.765	1.4621
0.4902	1.04560	−0.00277	10.272	−29.181	1.4600	0.4710	1.04595	−0.00237	14.406	−56.698	1.4608
0.5644	1.04033	−0.00291	12.819	−32.375	1.4582	0.5717	1.03869	−0.00261	22.727	−63.257	1.4584
0.6861	1.03147	−0.00284	22.739	−31.871	1.4552	0.6791	1.03073	−0.00256	36.837	−65.023	1.4556
0.7806	1.02433	−0.00243	33.483	−28.431	1.4530	0.7731	1.02359	−0.00226	56.870	−58.876	1.4535
0.8595	1.01815	−0.00182	46.836	−21.186	1.4510	0.8617	1.01664	−0.00166	84.586	−44.246	1.4512
0.9534	1.01051	−0.00071	67.335	−7.952	1.4485	0.9684	1.00789	−0.00046	132.066	−12.523	1.4484
		COP2 (1) + DMSO (2)						COP4 (1) + DMSO (2)			
		T/K = 298.15 K						T/K = 298.15			
0.0335	1.09440	−0.0003	2.485	−11.533	1.4775	0.0404	1.09233	−0.00016	2.574	−19.545	1.4774
0.0642	1.09342	−0.00048	3.003	−22.073	1.4772	0.0642	1.09055	−0.00026	2.977	−31.028	1.4770
0.1462	1.09100	−0.00112	4.442	−50.064	1.4764	0.1405	1.08495	−0.00062	4.808	−67.207	1.4754
0.2241	1.08870	−0.00173	7.596	−74.917	1.4754	0.2113	1.07984	−0.00099	7.527	−99.775	1.4740
0.3081	1.08620	−0.00235	12.099	−100.583	1.4743	0.2846	1.07453	−0.00131	11.670	−132.184	1.4725
0.4759	1.08080	−0.00322	29.233	−143.697	1.4716	0.4078	1.06572	−0.00186	23.717	−181.527	1.4697
0.4939	1.08014	−0.00325	32.218	−147.175	1.4714	0.4914	1.05972	−0.00213	37.188	−209.709	1.4678
0.5620	1.07778	−0.00344	45.963	−157.894	1.4703	0.5629	1.05456	−0.00230	53.599	−228.955	1.4662
0.6804	1.07320	−0.00334	83.304	−163.079	1.4681	0.6864	1.04544	−0.00227	102.237	−241.873	1.4631
0.7839	1.06873	−0.00282	138.934	−144.637	1.4660	0.7715	1.03899	−0.00203	160.964	−225.559	1.4612
0.8703	1.06452	−0.00194	210.161	−104.436	1.4642	0.8721	1.03112	−0.00140	271.413	−165.213	1.4586
0.9390	1.06101	−0.00107	284.274	−55.003	1.4627	0.9595	1.02402	−0.00052	422.220	−57.982	1.4563
		T/K = 313.15						T/K = 313.15			
0.0335	1.07883	−0.00027	1.862	−5.381	1.4706	0.0404	1.07661	−0.00017	1.929	−8.992	1.4703
0.0642	1.07806	−0.00056	2.221	−10.283	1.4703	0.0642	1.07491	−0.00025	2.211	−14.260	1.4698
0.1462	1.07583	−0.00116	3.522	−22.987	1.4694	0.1405	1.06959	−0.00062	3.442	−30.778	1.4685
0.2241	1.07381	−0.0018	5.280	−34.554	1.4685	0.2113	1.06475	−0.00099	5.149	−45.550	1.4671
0.3081	1.07155	−0.00242	8.066	−46.123	1.4674	0.2846	1.05979	−0.00140	7.723	−60.045	1.4655
0.4759	1.06667	−0.0033	17.864	−64.992	1.4649	0.4078	1.05146	−0.00199	14.794	−81.641	1.4632
0.4939	1.06608	−0.00333	19.737	−66.194	1.4646	0.4914	1.04584	−0.00235	22.642	−93.244	1.4613
0.5620	1.06387	−0.00348	27.057	−70.514	1.4636	0.5629	1.04097	−0.00256	31.957	−100.58	1.4600
0.6804	1.05966	−0.00338	46.985	−70.821	1.4616	0.6864	1.03226	−0.00253	57.569	−103.714	1.4571
0.7839	1.05553	−0.00287	74.144	−61.355	1.4596	0.7716	1.02602	−0.00220	86.907	−94.181	1.4551
0.8703	1.05163	−0.00202	106.531	−43.731	1.4579	0.8721	1.01848	−0.00156	136.345	−68.141	1.4527
0.9390	1.04831	−0.00111	139.838	−22.168	1.4564	0.9595	1.01158	−0.00058	200.006	−24.829	1.4505

to an oligomeric component of the copolymer, the *m*/*z* value and, in parenthesis, the EG and PG composition (in the order: "*n* + *p*" and "*m*") are indicated.

All of the peaks recorded in the mass spectra of the analyzed copolymers lead back to compounds having structure 1 with different values of *m*, *n*, and *p*; because no peaks due to

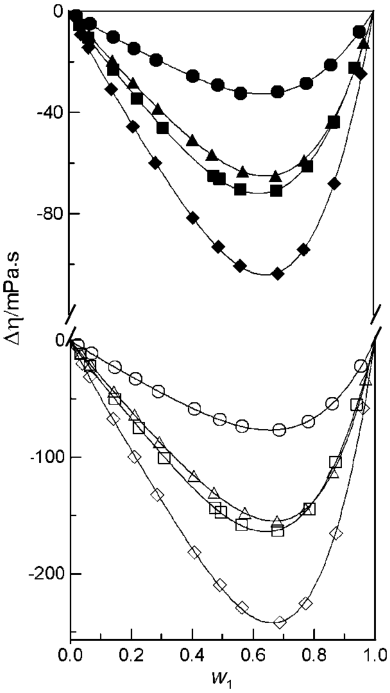

Figure 3. Deviation in viscosity, $\Delta\eta$, for the binary mixtures containing *block*-copolymers (1) + DMSO (2): (●,○), COP1 + DMSO; (■,□), COP2 + DMSO; (▲,△), COP3 + DMSO; (◆,◇), COP4 + DMSO. Open points, T/K = 298.15; full points, T/K = 313.15; full lines, eq 5.

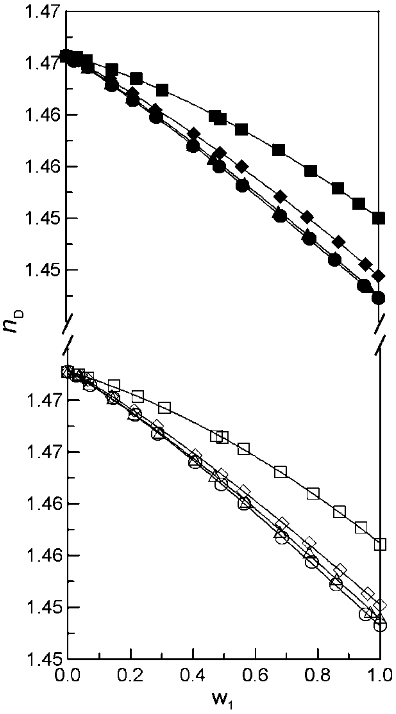

Figure 4. Refractive indices, n_D, versus the mass fraction, w_1, of the binary mixtures containing *block*-copolymers (1) + DMSO (2): (●,○), COP1 + DMSO; (■,□), COP2 + DMSO; (▲,△), COP3 + DMSO; (◆,◇), COP4 + DMSO. Open points, T/K = 298.15; full points, T/K = 313.15. Full lines correspond to a three-parameter polynomial regression.

impurities are found, COP1, COP2, COP3, and COP4 can be considered to be substantially pure.

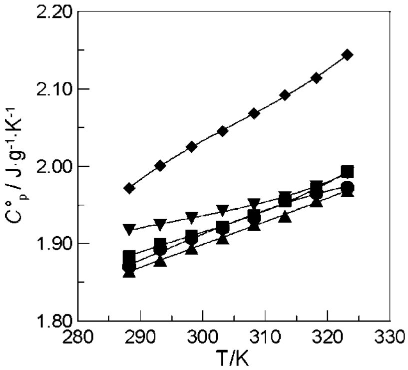

Figure 5. Heat capacities, C^0_p, of pure components in the range (288.15 to 333.15) K: ▲, COP1; ◆, COP2; ●, COP3; ■, COP4; ▼, DMSO; full line, eq 4.

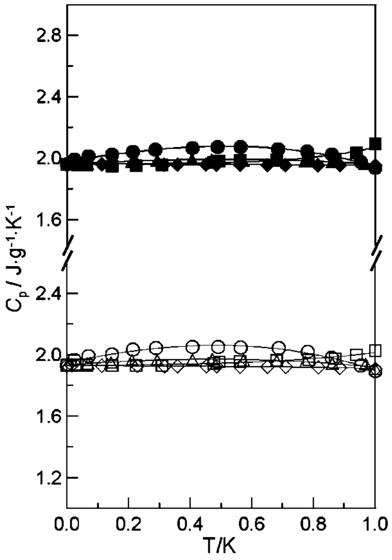

Figure 6. Heat capacities, C_p, for the binary mixtures containing *block*-copolymers (1) + DMSO (2): (●,○), COP1 + DMSO; (■,□), COP2 + DMSO; (▲,△), COP3 + DMSO; (◆,◇), COP4 + DMSO. Open points, T/K = 298.15; full points, T/K = 313.15; full lines, eq 4.

Table 4. Experimental Liquid Heat Capacities, C^0_p, of Pure Components under Atmospheric Pressure

T/K	COP1	COP2	COP3	COP4	DMSO
		C^0_p (J·g^{-1}·K^{-1})			
288.15	1.8642	1.9721	1.8708	1.8837	1.9179
293.15	1.8788	2.0015	1.8936	1.8995	1.9241
298.15	1.8944	2.0255	1.9075	1.9103	1.9333
303.15	1.9076	2.0455	1.9202	1.9217	1.9427
308.15	1.9246	2.0688	1.9338	1.9365	1.9505
313.15	1.9359	2.0921	1.9562	1.9552	1.9602
318.15	1.9553	2.1150	1.9660	1.9704	1.9743
323.15	1.9686	2.1449	1.9730	1.9935	1.9915

The average molecular weights of copolymers have been determined, by the use of Grams/386 program (PerSeptive Biosystem), from the corresponding MALDI mass spectra in the mass range 500 to 5000 (for COP1), 800 to 7500 (for COP2), 800 to 7500 (for COP3), and 1000 to 7500 (for COP4). The obtained values, slightly different than those given from the supplier, are reported in Table 2.

Measurement Techniques. Measurements of density, viscosity, refractive index, and heat capacity of the binary mixtures were carried out as previously reported.[1]

Density. The volume variation, ΔV (cm^3·g^{-1}), can be obtained by the following equation

$$\Delta V = 1/\rho - w_1/\rho_1 - w_2/\rho_2 \qquad (1)$$

where ρ is the density of the mixture and w_i and ρ_i (i = 1, 2) are the mass fraction and density of the ith component,

Table 5. Experimental Heat Capacities, C_p, for Binary Mixtures Containing *block*-Copolymers + DMSO

w_1	C_p / $\mathrm{J \cdot g^{-1} \cdot K^{-1}}$	w_1	C_p / $\mathrm{J \cdot g^{-1} \cdot K^{-1}}$
COP1 (1) + DMSO (2)			
T/K = 298.15			
0.0248	1.9671	0.4902	2.0528
0.0701	1.9919	0.5644	2.0493
0.1459	2.0028	0.6861	2.0444
0.2142	2.0347	0.7805	2.0217
0.2883	2.0448	0.8595	1.9829
0.4071	2.0503	0.9534	1.9289
T/K = 313.15			
0.0248	1.9930	0.4902	2.0729
0.0701	2.0126	0.5644	2.0715
0.1459	2.0240	0.6861	2.0584
0.2142	2.0401	0.7805	2.0438
0.2883	2.0564	0.8595	2.0254
0.4071	2.0659	0.9534	1.9747
COP2 (1) + DMSO (2)			
T/K = 298.15			
0.0335	1.9331	0.4939	1.9534
0.0642	1.9328	0.5620	1.9588
0.1462	1.9313	0.6804	1.9644
0.2241	1.9309	0.7839	1.9668
0.3081	1.9310	0.8703	1.9754
0.4759	1.9444	0.9390	1.9981
T/K = 313.15			
0.0335	1.9587	0.4939	1.9814
0.0642	1.9532	0.5620	1.9867
0.1462	1.9471	0.6804	1.9882
0.2241	1.9493	0.7839	1.9946
0.3081	1.9594	0.8703	1.9969
0.4759	1.9722	0.9390	2.0358
COP3 (1) + DMSO (2)			
T/K = 298.15			
0.0347	1.9374	0.4706	1.9703
0.0671	1.9424	0.5717	1.9648
0.1427	1.9515	0.6791	1.9627
0.2102	1.9647	0.7731	1.9558
0.2927	1.9653	0.8617	1.9429
0.4061	1.9698	0.9684	1.9399
T/K = 313.15			
0.0347	1.9620	0.4706	1.9900
0.0671	1.9653	0.5717	1.9869
0.1427	1.9731	0.6791	1.9845
0.2102	1.9787	0.7731	1.9829
0.2927	1.9842	0.8617	1.9774
0.4061	1.9937	0.9684	1.9645
COP4 (1) + DMSO (1)			
T/K = 298.15			
0.0161	1.9319	0.4851	1.9247
0.1133	1.9304	0.5618	1.9240
0.2272	1.9283	0.6505	1.9231
0.3157	1.9256	0.7093	1.9216
0.3589	1.9250	0.8150	1.9188
0.4518	1.9249	0.8858	1.9162
T/K = 313.15			
0.0161	1.9602	0.4851	1.9560
0.1133	1.9601	0.5618	1.9560
0.2272	1.9601	0.6505	1.9558
0.3157	1.9592	0.7093	1.9558
0.3589	1.9592	0.8150	1.9556
0.4518	1.9576	0.8858	1.9556

respectively. The experimental values for the four binary mixtures COP + DMSO are listed in Table 3. The curves of the volume variations, ΔV, versus the composition of these binary systems at the two experimental temperatures are shown in Figure 2.

Viscosity. The kinematic viscosities, ν ($\mathrm{cm^2 \cdot s^{-1}}$), were obtained from the equation

$$\nu = \eta/\rho = k(t - \theta) \qquad (2)$$

where η is the absolute (dynamic) viscosity, ρ is the density, k is the capillary constant, t is the flow time, and θ is the kinetic energy correction. In the whole set of experiments, we maintained flow times at > 200 s by selecting viscometers with appropriate values of k.

Equation 2 and the values of ρ allow calculation of the deviation in viscosity, $\Delta\eta$, from the definition

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

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

Values of $\Delta\eta$ are reported in Table 3 and plotted in Figure 3 against the mass fraction, w_1 of the polymers.

The uncertainty of the viscosity deviations was estimated to be less than 0.02 mPa·s.

Refractive Indices. Values of the refractive indices, fitted to a three-parameter polynomial, are reported in Table 3 and are plotted in Figure 4.

Heat Capacity. The experimental heat capacities, C^0_p, of pure components (from 288.15 to 323.15) K versus the temperature T/K at normal pressure are listed in Table 4 and represented in Figure 5. The experimental values of the heat capacities, C_p, of mixtures versus the mass fraction, w_1, of polymer are reported in Table 5 and represented in Figure 6. The expression used to fit C^0_p as a function of temperature is

$$C^0_p = c_o + c_1(T/\mathrm{K}) + c_2(T/\mathrm{K})^2 \qquad (4)$$

An analogous expression is used to fit C_p as a function of w_1: C^0_p and (T/K) in eq 4 are substituted by C_p and w_1, respectively.

Values of the parameters c_k (k = 0, 1, and 2) are listed in Tables 6 and 7 and together with the standard deviations $\sigma(C_p)$.

Results

Changes in volume variations, ΔV, and in deviation of viscosities, $\Delta\eta$, with composition can be expressed by the Redlich−Kister equation

Table 6. Adjustable Parameters of Equation *4* and Standard Deviation of Pure Components

component	c_0	c_1	c_2	$\sigma(C_p)$ / $\mathrm{J \cdot g^{-1} \cdot K^{-1}}$
COP1	1.273645	0.001214	0.000003	0.002
COP2	0.854869	0.003108	0.000003	0.003
COP3	−1.077079	0.001673	−0.000002	0.004
COP4	3.736256	−0.001485	0.000003	0.002
DMSO	3.948365	−0.015140	0.000003	0.002

Table 7. Adjustable Parameters of Equation *4* and Standard Deviation of *block*-Copolymers (1) + DMSO (2) at (298.15 and 313.15) K

T/K	c_0	c_1	c_2	$\sigma(C_p)$ / $\mathrm{J \cdot g^{-1} \cdot K^{-1}}$
COP1 (1) + DMSO (2)				
298.15	1.946478	0.501087	−0.542652	0.010
313.15	1.971843	0.437487	−0.457321	0.010
COP2 (1) + DMSO (2)				
298.15	1.933925	−0.030900	0.108596	0.008
313.15	1.959675	−0.065853	0.165569	0.016
COP3 (1) + DMSO (2)				
298.15	1.932898	0.163922	−0.176658	0.006
313.15	1.958244	0.128027	−0.126979	0.002
COP4 (1) + DMSO (2)				
298.15	1.931761	−0.010212	−0.008879	0.001
313.15	1.960864	−0.008768	0.0029073	0.001

Table 8. Adjustable Parameters, a_k, from Equation 5, and Standard Deviations, $\sigma(Q)$, from Equation 6, of *block*-Copolymers + DMSO at (298.15 and 313.15) K

function	T/K	a_0	a_1	a_2	$\sigma(Q)$
		COP1 (1) + DMSO (2)			
ΔV/cm^3·g^{-1}	298.15	−0.010616	−0.004507		0.000011
	313.15	−0.011454	−0.005402		0.000017
$\Delta\eta$/mPa·s	298.15	−275.6663	−184.9630	−77.6286	0.31
	313.15	−119.9231	−68.4009	−16.8866	0.43
		COP2 (1) + DMSO (2)			
ΔV/cm^3·g^{-1}	298.15	−0.013195	−0.005838		0.000026
	313.15	−0.013496	−0.005812		0.000026
$\Delta\eta$/mPa·s	298.15	−595.8865	−366.9429	−119.3091	1.32
	313.15	−268.1115	−141.9873	−28.6819	0.66
		COP3 (1) + DMSO (2)			
ΔV/cm^3·g^{-1}	298.15	−0.011484	−0.004890		0.000022
	313.15	−0.009905	−0.005313		0.000028
$\Delta\eta$/mPa·s	298.15	−546.2766	−398.3391	−197.9035	0.94
	313.15	−236.7417	−147.9439	−55.9200	0.25
		COP4 (1) + DMSO (2)			
ΔV/cm^3·g^{-1}	298.15	−0.008686	−0.005063		0.000014
	313.15	−0.009464	−0.005983		0.000021
$\Delta\eta$/mPa·s	298.15	−854.5760	−612.3870	−279.6565	2.43
	313.15	−378.6496	−237.2606	−91.4585	0.56

$$Q_{\text{calcd}} = w_1 w_2 \sum_{k\geq 0} a_k (w_1 - w_2)^k \qquad (5)$$

where Q_{calcd} refers to ΔV or $\Delta\eta$. The adjustable parameters a_k were determined by a least-squares method. The corresponding results are reported in Table 8. The tabulated standard deviations, $\sigma(Q)$, reported in the same Table, are defined as

$$\sigma(Q) = \left|\xi_{\min}/(N-n)\right|^{0.5} \qquad (6)$$

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

$$\xi = \sum_{k=1}^{N} (Q_{\text{calcd}} - Q)^2 \qquad (7)$$

and Q is the experimental value.

Discussion

As can be seen from Figure 2, the volume variations, ΔV, are small and always negative. The effect of temperature on ΔV is insignificant, whereas the copolymers show an increase in ΔV with increasing molecular weight, M_n.

Although the small values of ΔV of COPs in DMSO cannot encourage any decisive conclusion, the experimental evidence indicates a small increase in ΔV and a larger decrease in $\Delta\eta$ when the molecular size of the polymer is increased.

ΔV and $\Delta\eta$ values of the same order are observed in mixtures of polypropylene glycols (PPG) in 2-methyltetrahydrofuran (MTHF).[1]

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