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Densities, Viscosities, Refractive Indices, and Heat Capacities of Poly(ethylene glycol-*ran*-propylene glycol) + Esters of Carbonic Acid at (293.15 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 poly(ethylene glycol-*ran*-polypropylene glycol) + esters of carbonic acid were determined at (293.15 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

Studies in thermodynamic and bulk properties of binary mixtures are being increasingly used as tools for the investigation of the properties of pure components and the nature of intermolecular interactions between the liquid mixture constituents.

This paper continues our systematic studies for determination of the thermodynamic properties of binary mixtures containing glycols, polyglycols, and copolymers as one component.[1−4]

Here, we present experimental data of densities, ρ, dynamic viscosities, η, refractive indices, n_D (sodium line), and heat capacities, C_p, of the binary mixtures containing poly(ethylene glycol-*ran*-propylene glycol) (COP) + three esters of carbonic acid, namely, dimethyl carbonate (DMC), diethyl carbonate (DEC), and propylene carbonate (PC). Measurements were determined at (293.15 and 313.15) K and at normal pressure. The copolymer (COP) was chosen because of its wide range of industrial applicability in hydraulic fluids, heat transfer fluids, lubricants, solvents, plasticizers, and foam control agents.

Esters of carbonic acid are attracting an increasing interest due to their uses in extractions of industrial importance, such as the production of many synthetic and natural resins and polymers,[5] in the synthesis of pharmaceuticals,[6] in agricultural chemistry, and as fuel additives.[7] Particularly, there is a high interest in the dimethyl carbonate and propylene carbonate applications to storage batteries,[8,9] based on intercalation of solutions of carbonates with lithium and bromine in graphite. Such batteries can be recharged thermally at relatively low temperatures.

Binary mixtures containing propylene carbonate and other organic solvents, especially aprotic ones, have also a great technological and theoretical interest.[10]

The thermodynamic properties of COP + esters of carbonic acid depend mostly on the interactions between the −OH terminal groups of the copolymer and the −COOR groups of esters.

Densities, viscosities, refractive indices, and heat capacities were measured experimentally using standard techniques. From density and viscosity values, the volume variation, ΔV, and the deviation in viscosity, $\Delta\eta$, were calculated. The Redlich−Kister equation was used to correlate the experimental data and the standard deviations, σ, between experimental and calculated values. No data on the binary mixtures studied in this paper were found in the literature.

Experimental Section

Materials. All chemicals were from Aldrich and were used without further purification. COP shows a nominal molecular weight $M_n = 2500$, and its characterization is reported below.

DMC (anhydrous ≥ 99 %), DEC (anhydrous ≥ 99 %), and PC (anhydrous ≥ 99.7 %) were degassed ultrasonically (ultrasonic bath, Hellma, type 460, Milan, Italy) and dried over freshly activated molecular sieves (Fluka, type 4 Å) for several days to remove any traces of moisture. The pure components were also kept in an inert argon atmosphere as soon as the bottles were used. The purity of liquids was confirmed by GLC analysis.[1]

Experimental values of densities, ρ, dynamic viscosities, η, refractive indices, n_D, and heat capacities, C_p, of the pure liquids were reported in Table 1 and compared with available literature data,[11−22] where possible.

^{1}H NMR Analysis. ^{1}H NMR spectra were obtained on an AC 200 F Bruker spectrometer interfaced with an Aspect 3000 computer, using the Bruker DISR 90 acquisition software. Samples were dissolved in $CDCl_3$ and the chemical shifts expressed in parts per million by comparison with the signal of TMS used as an internal standard.

MALDI-TOF Mass Spectrometric Analysis. MALDI-TOF mass spectra of the copolymer sample were acquired by a 4800

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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

		$\rho/g \cdot cm^{-3}$		$\eta/mPa \cdot s$		n_D		$C_p/J \cdot g^{-1} \cdot K^{-1}$	
	T/K	this paper	lit.	this paper	lit.	this paper	lit.	this paper	lit.
COP	293.15	1.09306		629.534		1.4667		2.041	
	313.15	1.07681		295.555		1.4596		2.151	
DMC	293.15	1.06980	1.06969[a] 1.06954[d] 1.0700[e]	0.629	0.623[a] 0.6173[d]	1.3689	1.3687[b]	1.844	1.734[c]
	313.15	1.04325	1.043105[a] 1.04301[d] 1.0434[e]	0.494	0.494[f] 0.4807[d] 0.486[a]	1.3604		1.896	1.808[c]
DEC	293.15	0.97584	0.97500[g] 0.9747[h]	0.817	0.810[h]	1.3858	1.3852[i]	1.790	1.861[c]
	313.15	0.95239	0.95232[g] 0.9522[h]	0.623	0.625[h]	1.3764		1.827	1.907[c]
PC	293.15	1.20466		2.778	2.770[l]	1.4223		1.645	1.705[c]
	313.15	1.18306	1.1836[m]	1.909		1.4149	1.4158[n]	1.706	1.742[c]

[a] Ref 11. [b] Ref 12. [c] Ref 13. [d] Ref 14. [e] Ref 15. [f] Ref 16. [g] Ref 17. [h] Ref 18. [i] Ref 19. [l] Ref 20. [m] Ref 21. [n] Ref 22.

Proteomics analyzer MALDI time-of-flight/time-of-flight mass spectrometer (Applied Biosystems, Framingham, MA) in reflectron mode and in positive polarity. The samples were prepared by mixing about 0.1 mmol of polymer and 40 mmol of *trans*-3-indoleacrylic acid (used as a matrix) on the sampler target, using tetrahydrofurane doped with NaCl (as cationizing agent) as a solvent. After instrument calibration, the number average, M_n ($= \Sigma N_i M_i / \Sigma N_i$), and the weight average, M_w ($= \Sigma N_i M_i^2 / \Sigma N_i M_i = \Sigma w_i M_i$), molecular masses were determined using the Grams/386 program (PerSeptive Biosystem) applied on spectra corrected for the offset and the baseline.[23] In the above equalities, N_i is the number of moles of species i, having molecular mass M_i and weight fraction w_i. The polydispersity index was also obtained as the ratio M_w/M_n.

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 can be obtained by the following equation

$$\Delta V = 1/\rho - w_1/\rho_1 - w_2/\rho_2 \tag{1}$$

where ρ is the density of the mixture, w_i, and ρ_i ($i = 1, 2$) are the mass fractions and densities of the ith component, respectively. The experimental values for the four binary mixtures COP + esters of carbonic acids are listed in Table 2. The uncertainty in the densities was $\pm\ 1.5 \cdot 10^{-5}$ g·cm^{-3}. Correspondingly, the uncertainty in the volume variation, ΔV, is estimated as < 1 %. The curves of the volume variations, ΔV, vs the composition of these binary systems at the two experimental temperatures are shown in Figure 2.

Viscosity. The viscosities were obtained from the kinematic viscosities, ν, from the equation

$$\eta = \upsilon\rho = k(t - \theta)/\rho \tag{2}$$

where η is 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, flow times were maintained > 200 s, by selecting viscometers with appropriate values of k. On this subject, the capillary diameters of the viscometers, varying from 0.47 mm up to 2.65 mm, were used for kinematic ranges of (0.5 to 300) mm^2·s^{-1}, respectively. The viscometers were filled with 15 cm^3 of solution for each measurement. The calibration of the viscometers was carried out with double distilled water and by a standard oil specimen of known viscosity (Petrotest, DIN 51 550). 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, mass fraction, and calibration fluid. So, according to the precision of all experimental instruments, the experimental average uncertainties of kinematic viscosity were estimated to be ± 0.01 cm^2·s^{-1}.

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

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

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 2 and plotted in Figure 3 against the mass fraction, w_1, of the copolymer. The uncertainty of the viscosity deviations was estimated to be less than 0.02 mPa·s.

Refractive Indices. Values of the refractive indices (sodium line), fitted to a three parameter polynomial, are reported in Table 2 and plotted in Figure 4.

Heat Capacity. The experimental heat capacities, C^0_p, of pure components from (288.15 to 323.15) K vs the temperature T/K, at normal pressure, are listed in Table 3 and represented in Figure 5. The experimental values of the heat capacities, C_p, of mixtures vs the mass fraction, w_1, of polymer are reported in Table 4 and represented in Figure 6. The expression used to fit C^0_p as a function of temperature is

$$C^0_p = c_0 + c_1(T/\mathrm{K}) + c_2(T/\mathrm{K})^2 \tag{4}$$

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 5 and 6 together with the standard deviations σ (C_p).

Characterization of the Copolymer

Poly(ethylene glycol-*ran*-propylene glycol) (COP) is a random copolymer having the following general Structure I

$$HO{-}({-}CH_2{-}CH_2{-}O{-})_n{-}[{-}CH(CH_3){-}CH_2{-}O{-}]_m{-}H$$

(Structure I)

The relative abundance of ethylene glycol (E.G., $-CH_2-CH_2-O-$) and propylene glycol [P.G., $-CH(CH_3)-CH_2-O-$] units in the copolymer sample has been achieved by ^{1}H NMR analysis. In the spectrum (omitted for brevity), two clusters of signals are present between (1.0 and 1.2) ppm (due to the CH_3 group of P.G.) and between (3.3 and 3.8) ppm (due to CH_2 groups of P.G. and E.G. and to a CH group of P.G.); on the

Table 2. Densities, ρ, Volume Variations, ΔV, Dynamic Viscosities, η, Deviations in Dynamic Viscosities, $\Delta\eta$, and Refractive Indices, n_D, of COP + Esters of Carbonic Acid at (293.15 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
COP (1) + DMC (2)					
T/K = 293.15					
0.0259	1.07070	−0.00026	0.784	−16.13	1.3712
0.0530	1.07164	−0.00054	0.936	−33.06	1.3741
0.1199	1.07386	−0.00113	1.565	−74.47	1.3810
0.1990	1.07650	−0.00183	2.730	−123.08	1.3890
0.2925	1.07941	−0.00246	5.049	−179.51	1.3983
0.4243	1.08313	−0.00300	11.717	−255.76	1.4115
0.4936	1.08483	−0.00306	21.243	−289.78	1.4183
0.5934	1.08715	−0.00303	34.072	−339.73	1.4280
0.6957	1.08927	−0.00276	64.121	−374.02	1.4380
0.7862	1.09087	−0.00229	120.398	−374.69	1.4466
0.8739	1.09221	−0.00166	235.987	−314.22	1.4550
0.9505	1.09296	−0.00076	433.589	−164.79	1.4622
T/K = 313.15					
0.0259	1.04450	−0.00037	0.607	−7.53	1.3627
0.0530	1.04581	−0.00076	0.763	−15.38	1.3655
0.1199	1.04888	−0.00156	1.251	−34.62	1.3724
0.1990	1.05241	−0.00239	2.099	−57.12	1.3804
0.2925	1.05634	−0.00314	3.743	−83.05	1.3900
0.4243	1.06147	−0.00378	8.219	−117.47	1.4032
0.4935	1.06395	−0.00390	12.352	−133.77	1.4102
0.5934	1.06719	−0.00378	22.064	−153.51	1.4200
0.6957	1.07027	−0.00341	40.532	−165.23	1.4302
0.7862	1.07262	−0.00275	69.092	−163.39	1.4391
0.8739	1.07447	−0.00174	124.515	−133.82	1.4475
0.9505	1.07594	−0.00073	209.126	−71.81	1.4549
COP (1) + DEC (2)					
T/K = 293.15					
0.0836	0.98511	−0.00045	1.485	−51.91	1.3920
0.1546	0.99330	−0.00103	2.451	−95.56	1.3976
0.2017	0.99881	−0.00140	3.343	−124.31	1.4013
0.3097	1.01154	−0.00213	6.750	−188.80	1.4097
0.3904	1.02104	−0.00247	11.306	−234.94	1.4161
0.4608	1.02936	−0.00264	17.712	−272.82	1.4218
0.5237	1.03674	−0.00264	26.366	−303.72	1.4268
0.6253	1.04865	−0.00243	51.351	−342.59	1.4351
0.7019	1.05776	−0.00222	85.913	−356.23	1.4414
0.8219	1.07214	−0.00171	212.678	−304.91	1.4512
0.8931	1.08064	−0.00123	337.947	−224.37	1.4573
0.9567	1.08812	−0.00060	494.274	−108.05	1.4628
T/K = 313.15					
0.0836	0.96271	−0.00110	1.093	−24.19	1.3829
0.1546	0.97160	−0.00200	1.746	−44.47	1.3886
0.2017	0.97755	−0.00254	2.327	−57.80	1.3924
0.3097	0.99104	−0.00337	4.415	−87.56	1.4015
0.3904	1.00126	−0.00388	7.038	−108.72	1.4081
0.4608	1.00998	−0.00396	10.543	−125.99	1.4140
0.5237	1.01777	−0.00390	15.141	−139.95	1.4192
0.6253	1.03031	−0.00355	27.120	−157.92	1.4277
0.7019	1.03973	−0.00304	43.100	−164.55	1.4343
0.8219	1.05452	−0.00196	88.987	−154.05	1.4446
0.8931	1.06330	−0.00117	141.529	−122.50	1.4507
0.9567	1.07135	−0.00051	217.993	−64.80	1.4562
COP (1) + PC (2)					
T/K = 293.15					
0.0681	1.19696	−0.00043	4.985	−40.04	1.4255
0.1271	1.19078	−0.00110	7.826	−74.18	1.4286
0.2097	1.18226	−0.00204	14.152	−119.68	1.4327
0.2736	1.17557	−0.00264	21.782	−152.14	1.4359
0.3436	1.16806	−0.00311	34.112	−183.69	1.4393
0.4162	1.16006	−0.00336	51.039	−212.32	1.4428
0.4466	1.15667	−0.00340	63.517	−218.89	1.4440
0.5862	1.14080	−0.00322	130.926	−239.09	1.4503
0.6431	1.13432	−0.00302	172.974	−232.71	1.4528
0.7562	1.12144	−0.00249	274.680	−201.92	1.4574
0.8621	1.10945	−0.00182	395.529	−147.51	1.4617
0.9337	1.10114	−0.00196	505.993	−81.98	1.4644
T/K = 313.15					
0.0681	1.17621	−0.00076	3.258	−18.65	1.4183
0.1271	1.17007	−0.00121	4.886	−34.33	1.4213
0.2097	1.16187	−0.00207	8.301	−55.18	1.4253
0.2736	1.15545	−0.00262	12.138	−70.12	1.4285
0.3436	1.14846	−0.00319	17.939	−84.86	1.4319
0.4162	1.14111	−0.00364	26.172	−97.95	1.4354
0.4466	1.13803	−0.00380	31.099	−101.94	1.4368
0.5862	1.12358	−0.00415	59.972	−114.09	1.4430
0.6431	1.11755	−0.00409	78.028	−112.73	1.4455
0.7562	1.10537	−0.00365	123.143	−100.82	1.4502
0.8621	1.09350	−0.00267	184.190	−70.87	1.4545
0.9337	1.08506	−0.00153	233.682	−42.42	1.4570

Table 3. Experimental Liquid Heat Capacities, C^0_p, of Pure Components at Atmospheric Pressure

T/K	COP	DMC	DEC	PC
	C^0_p ($J \cdot g^{-1} \cdot K^{-1}$)			
288.15	1.993	1.837	1.779	1.629
293.15	2.041	1.844	1.790	1.645
298.15	2.100	1.855	1.799	1.660
303.15	2.144	1.870	1.810	1.673
308.15	2.155	1.884	1.819	1.687
313.15	2.155	1.896	1.827	1.706
318.15	2.146	1.911	1.850	1.723
323.15	2.123	1.928	1.865	1.738

Table 4. Experimental Heat Capacities, C_p, for Binary Mixtures Containing COP + Esters of Carbonic Acid

w_1	C_p / $J \cdot g^{-1} \cdot K^{-1}$	w_1	C_p / $J \cdot g^{-1} \cdot K^{-1}$
COP (1) + DMC (2)			
T/K = 293.15			
0.0259	1.851	0.4936	1.912
0.0530	1.852	0.5934	1.932
0.1199	1.858	0.6957	1.956
0.1990	1.868	0.7862	1.978
0.2925	1.878	0.8739	2.003
0.4243	1.900	0.9505	2.025
T/K = 313.15			
0.0259	1.899	0.4936	1.995
0.0530	1.902	0.5934	2.024
0.1199	1.915	0.6957	2.055
0.1990	1.932	0.7862	2.087
0.2925	1.958	0.8739	2.106
0.4243	1.989	0.9505	2.136
COP (1) + DEC (2)			
T/K = 293.15			
0.0836	1.805	0.5237	1.895
0.1546	1.815	0.6253	1.927
0.2017	1.826	0.7019	1.944
0.3097	1.856	0.8219	1.975
0.3904	1.866	0.8931	2.004
0.4608	1.890	0.9567	2.025
T/K = 313.15			
0.0836	1.846	0.5237	1.971
0.1546	1.863	0.6253	2.005
0.2017	1.876	0.7019	2.032
0.3097	1.905	0.8219	2.075
0.3904	1.939	0.8931	2.106
0.4608	1.955	0.9567	2.136
COP (1) + PC (2)			
T/K = 293.15			
0.0681	1.666	0.4466	1.797
0.1271	1.685	0.5862	1.856
0.2097	1.716	0.6431	1.880
0.2736	1.733	0.7562	1.926
0.3436	1.763	0.8621	1.975
0.4162	1.785	0.9337	2.010
T/K = 313.15			
0.0681	1.726	0.4466	1.880
0.1271	1.748	0.5862	1.940
0.2097	1.780	0.6431	1.966
0.2736	1.805	0.7562	2.021
0.3436	1.836	0.8621	2.075
0.4163	1.860	0.9337	2.110

basis of the intensities of these signals, the values of [*n*] (% mol E.G. component abundance) and [*m*] (% mol P.G. component abundance) have been determined. The obtained results are reported in Table 7.

The chemical characterization of the copolymer, to determine both average molecular mass and microstructure, has been attempted by MALDI-TOF mass spectrometry.

In a previous work,[4] because of the lower molecular mass of polymeric samples investigated, the interpretation of mass

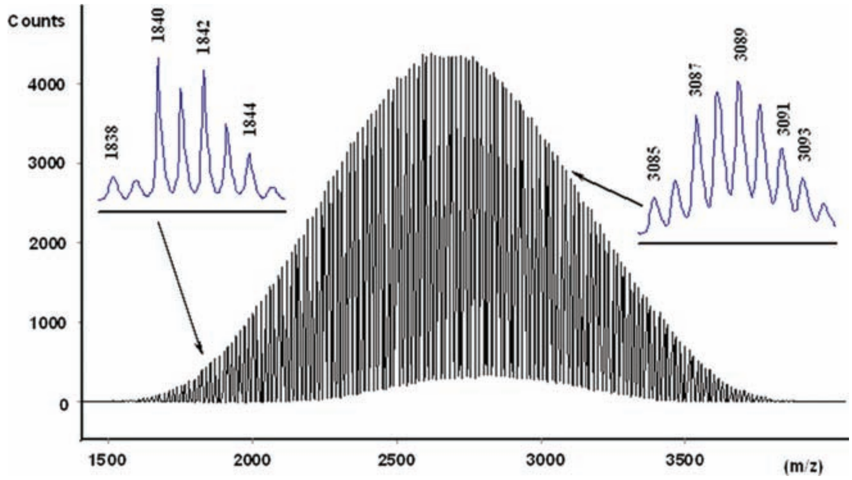

Figure 1. Positive MALDI-TOF mass spectrum of COP. In the insets, on the top of each peak due to an oligomeric species present in the copolymer, the rounded *m*/*z* value is indicated. The composition (in the order, "*n*" and "*m*", see Structure I) is given in the following: *m*/*z* 1838 (25, 12), *m*/*z* 1840 (29, 9), *m*/*z* 1842 (4, 28; 33, 6), *m*/*z* 1844 (8, 25; 37, 3), *m*/*z* 3085 (23, 35; 52, 13), *m*/*z* 3087 (27, 32; 56, 10), *m*/*z* 3089 (2, 51; 31, 29; 60, 7), *m*/*z* 3091 (6, 48; 35, 26; 64, 4), *m*/*z* 3093 (10, 45; 39, 23; 68, 1).

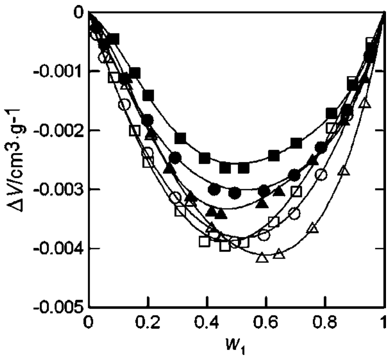

Figure 2. Volume variations, ΔV, for the binary mixtures containing COP (1) + esters of carbonic acid (2): ●,○, COP + DMC; ■,□, COP + DEC; ▲,Δ, COP + PC. Full points, T/K = 293.15; open points, T/K = 313.15. Full lines, eq 5.

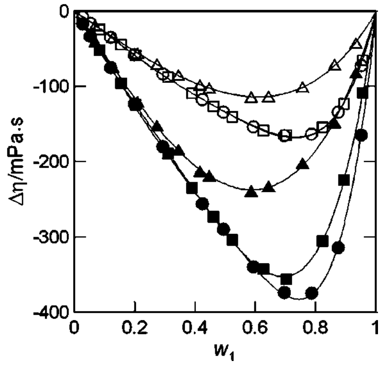

Figure 3. Deviation in viscosity, $\Delta\eta$, for the binary mixtures containing COP (1) + esters of carbonic acid (2): ●,○, COP + DMC; ■,□, COP + DEC; ▲,Δ, COP + PC. Full points, T/K = 293.15; open points, T/K = 313.15. Full lines, eq 5.

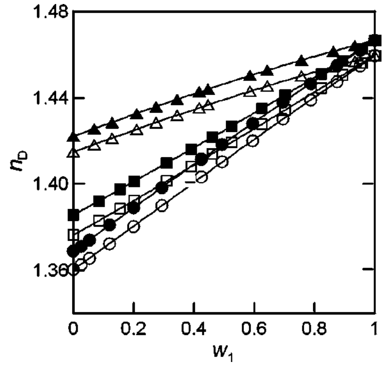

Figure 4. Refractive indices, n_D, vs the mass fraction, w_1, of the binary mixtures containing COP (1) + esters of carbonic acid (2): ●,○, COP + DMC; ■,□, COP + DEC; ▲,Δ, COP + PC. Full points, T/K = 293.15; open points, T/K = 313.15. Full lines correspond to a three parameter polynomial regression.

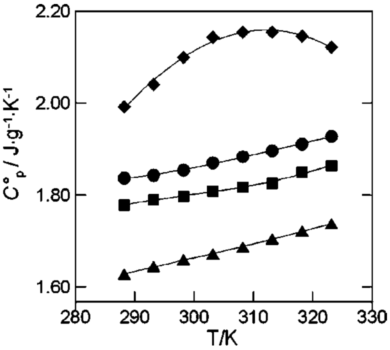

Figure 5. Heat capacities, C^0_p, of pure components in the range (288.15 to 323.15) K. ◆, ●, ■, ▲ refer to COP, DMC, DEC, and PC, respectively. Full line, eq 4.

spectra was made rounding the atomic mass of C, H, and O to 12, 1, and 16, respectively. In the present case, in consequence of the high mass of COP, the correct attribution of peaks present in its mass spectrum can be obtained only by determining the exact mass of oligomers having Structure I. So, considering that the exact mass of the most abundant isotope of C, H, and O is 12.0000, 1.0078, and 15.9949, respectively, the molecular masses of repeating units result, E.G. = 44.026 and P.G. = 58.042; consequently, molecular masses of macromolecules constituting COP, cationized with Na^+, will be given from the following equation

$$m/z = (18.011 + 22.990) + n \cdot 44.026 + m \cdot 58.042$$

Accordingly, the mass spectrum of COP, reported in Figure 1, shows a series of peaks whose masses, included between ≈ *m*/*z* 1500 and ≈ *m*/*z* 4000, correspond to those expected.

Although each signal of the overall mass spectrum looks like a single peak, it is really constituted of a cluster of peaks due not only to the isotopic pattern of different compounds but

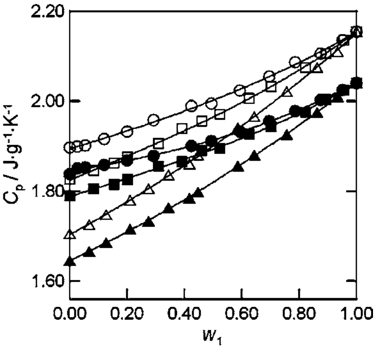

Figure 6. Heat capacities, C_p, for the binary mixtures containing COP (1) + esters of carbonic acid (2): ●,○, COP + DMC; ■,□, COP + DEC; ▲,Δ, COP + PC. Full points, T/K = 293.15; open points, T/K = 313.15. Full lines, eq 4.

Table 5. Adjustable Parameters of Equation 4 and Standard Deviation of Pure Components

component	c_0	c_1	c_2	$\sigma(C_p)$ J·g^{-1}·K^{-1}
COP	−27.0693882	0.1873377	−0.0003002	0.0071
DMC	2.9823099	−0.0098881	0.0000205	0.0018
DEC	3.9643096	−0.0164375	0.0000308	0.0034
PC	1.6204181	−0.0027068	0.0000095	0.0016

Table 6. Adjustable Parameters of Equation 4 and Standard Deviation of COP (1) + Esters of Carbonic Acid (2) at (293.15 and 313.15) K

T/K	c_0	c_1	c_2	$\sigma(C_p)$ J·g^{-1}·K^{-1}
		COP (1) + DMC (2)		
293.15	1.845114	0.080629	0.113824	0.0029
313.15	1.894952	0.171387	0.086091	0.0039
		COP (1) + DEC (2)		
293.15	1.790979	0.161799	0.085071	0.0039
313.15	1.826795	0.227585	0.097231	0.0035
		COP (1) + PC (2)		
293.15	1.645531	0.301647	0.093920	0.0019
313.15	1.704250	0.337814	0.108502	0.0027

mostly to the presence of oligomers of different compositionswhose masses differ by about 2 amu. This fact is well evidenced in the insets of Figure 1 (enlargements of the zone of the spectrum included between m/z 1837 and 1846 and between m/z 3084 and 3094) in which, on the top of each peak due to an oligomeric component of the copolymer, the rounded m/z value and, in the captions, the E.G. and P.G. composition (in the order: "n" and "m") are indicated.

Remarkably, referring to the first inset, for peaks at m/z 1842 and m/z 1844, two different compositions are reported because, owing to the high average molecular mass of COP, isobaries are possible (on the contrary, each one of the other two peaks is associable to only one oligomer). So, for example, the peak at m/z 1842 can be generated from the two following species

$$HO{-}({-}CH_2{-}CH_2{-}O{-})_{33}{-}[{-}CH(CH_3){-}CH_2{-}O{-}]_6{-}H\ Na^+$$

m/z 1842.111

$$HO{-}({-}CH_2{-}CH_2{-}O{-})_4{-}[{-}CH(CH_3){-}CH_2{-}O{-}]_{28}{-}H\ Na^+$$

m/z 1842.281

which, although with a different probability, are both present in the copolymer sample. Because the instrument resolution, at these mass values, is not sufficient to discriminate peaks which differ by less than one amu, they are recorded as a single signal.

The higher the masses are, the more numerous the isobaries became; for example, the peak at m/z 3089 corresponds to three different oligomers [$n = 2$ and $m = 51$ (m/z 3089.195), $n = 31$ and $m = 29$ (m/z 3089.025), $n = 60$ and $m = 7$ (m/z 3088.855)], while the one at m/z 4400 corresponds to four [$n = 12$ and $m = 66$ (m/z 4400.085), $n = 41$ and $m = 44$ (m/z 4399.915), $n = 70$ and $m = 22$ (m/z 4399.745), $n = 99$ and $m = 0$ (m/z 4399.575)].

However, all peaks recorded in the mass spectrum of the analyzed copolymer are leading back to compounds having Structure I, with different values of "n" and "m"; because no peaks due to impurities are found, COP can be considered substantially pure.

The average molecular mass of COP (both M_n and M_w) has been determined, using the Grams/386 program (PerSeptive Biosystem), from the corresponding positive MALDI mass spectrum in the mass range 500 to 10000. The obtained values are reported in Table 7.

Table 7. Chemical Composition and Average Molecular Mass of COP

sample	E.G. mol % (wt. %) (our data)	P.G. mol % (wt. %) (our data)	M_n (Aldrich)	M_n (our data)	M_w (our data)	M_w/M_n (our data)
COP	79.7 (74.9)	20.3 (25.1)	~ 2500	2676	2730	1.020

Table 8. Adjustable Parameters, a_k, from Equation 5, and Standard Deviations $\sigma(Q)$, from Equation 6, of COP + Esters of Carbonic Acid at (293.15 and 313.15) K

function	T/K	a_0	a_1	a_2	a_4	$\sigma(Q)$
			COP (1) + DMC (2)			
ΔV/cm^3·g^{-1}	293.15	−0.012312	−0.000919	−0.001112	−0.003030	0.000019
	313.15	−0.015620	−0.001270	0.000198	0.000959	0.000028
$\Delta\eta$/mPa·s	293.15	−1169.655	−1027.166	−1071.651	−701.606	2.37
	313.15	−535.674	−434.474	−421.491	−284.865	1.39
			COP (1) + DMC (2)			
ΔV/cm^3·g^{-1}	293.15	−0.010512	0.0002421	0.001306	−0.006827	0.000017
	313.15	−0.0158231	0.001980	0.003461	−0.0008456	0.000036
$\Delta\eta$/mPa·s	293.15	−1177.984	−1006.784	−577.201	−72.107	2.05
	313.15	−534.128	−424.514	−417.932	−307.039	1.61
			COP (1) + PC (2)			
ΔV/cm^3·g^{-1}	293.15	−0.013072	0.002195	0.001570	−0.010948	0.000016
	313.15	−0.015908	−0.006160	−0.002022	−0.002430	0.000042
$\Delta\eta$/mPa·s	293.15	−918.754	−322.262	−53.659	−113.743	2.04
	313.15	−432.721	−190.803	−51.191	−26.932	0.92

Results

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

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

where Q_{calc} 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

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

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

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

and Q is the experimental value.

Discussion

As can be seen from experimental data of Table 2 and Figure 2, the variations in densities, ΔV, for the binary mixtures COP + esters of carbonic acid are always negative. This is due to a volume contraction on mixing correlated, probably, to several effects, such as interactions between COP molecules and esters of carbonic acid and steric hindrance. The ΔV values of the binary mixtures follow the order DEC > DMC > PC, although the observed variations are quite small.

The viscosity deviations, $\Delta\eta$, present negative values over the whole mass fraction range at T = (293.15 and 313.15) K. They become less negative following the sequence DMC < DEC < PC at 293.15 K, whereas at T = 313.15 K they follow the order DMC ≅ DEC < PC. $\Delta\eta$ values decrease with increasing temperature. All values of refractive indices, n_D, and heat capacities, C_p, are always positive. Values of n_D decrease in the order PC > DEC > DMC, while for C_p, the order becomes DMC > DEC > PC.

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