614 *J. Chem. Eng. Data* **1997,** *42,* 614−618

Densities, Relative Permittivities, and Refractive Indices for the Binary Liquid System Propylene Carbonate + *p*-Xylene at (15, 20, 25, 30, and 35) °C

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Densities, relative permittivities, and refractive indices of propylene carbonate + *p*-xylene mixtures at (15, 20, 25, 30, and 35) °C were measured. Excess molar volumes were calculated, as well as deviations in relative permittivity and molar refraction. All the above quantities were found to be negative.

Introduction

Dipolar, aprotic solvents are used in many chemical or electrochemical applications as media where various reactions take place. One of these solvents is propylene carbonate, which is widely used as a nonaqueous electrolyte in high-energy lithium batteries (Gabano, 1983). Thermophysical properties of binary liquid mixtures with propylene carbonate are systematically studied in our laboratory (Moumouzias et al., 1991; Moumouzias and Ritzoulis, 1992).

This paper is part of a general work studying the physicochemical properties and the intermolecular interactions in mixtures of propylene carbonate with aromatic hydrocarbons. Here, density, relative permittivity and refractive index measurements of propylene carbonate + *p*-xylene mixtures at (15, 20, 25, 30, and 35) °C are reported. Excess molar volumes and deviations in relative permittivity and in molar refractivity are also calculated.

Experimental Section

Propylene carbonate (Merck, >99%) was treated by distillation, and the middle part was collected. Before distillation it was stored in a flask with molecular sieves (5 Å) for at least 24 h. *p*-Xylene (Fluka, puriss p.a. >99%) was fractionally distilled twice, and the middle fraction of the second distillation was collected.

All solutions were prepared by mass, with a Shimadzu AEG-220 analytical balance of four decimal places. The solutions were prepared under a dry nitrogen atmosphere. Corrections for the weight in air to that in vacuum were taken into account. The error in the mole fraction was estimated to be lower than ±0.000 03. The atomic masses were taken from the atomic mass table of IUPAC (1986).

Density measurements were made with an Anton-Paar DMA (measuring cell 602 and processing unit 60) vibrating tube densimeter, which was calibrated with air and double-distilled water. The temperature was regulated by a Haake F3-K Digital thermostat with a stability of ±0.02 deg and measured by a DT 100-30 Anton-Paar digital thermometer. The accuracy in density values was better than $\pm 5 \times 10^{-5}$ g cm^{-3} and in excess volume values ±0.007 cm^3 mol^{-1}.

Permittivities were measured with a Wissenschaftlich Technische Werkstatten GmbH, model WTW DM-01, dipolmeter. A YSI (model 72) thermostat with a stability of ±0.005 deg was used to regulate the temperature of the dipolmeter's cell. The dipolmeter was calibrated with carbon tetrachloride, benzene, chlorobenzene, 1,2-dichloroethane, benzyl alcohol, nitrobenzene, and water, in accor-

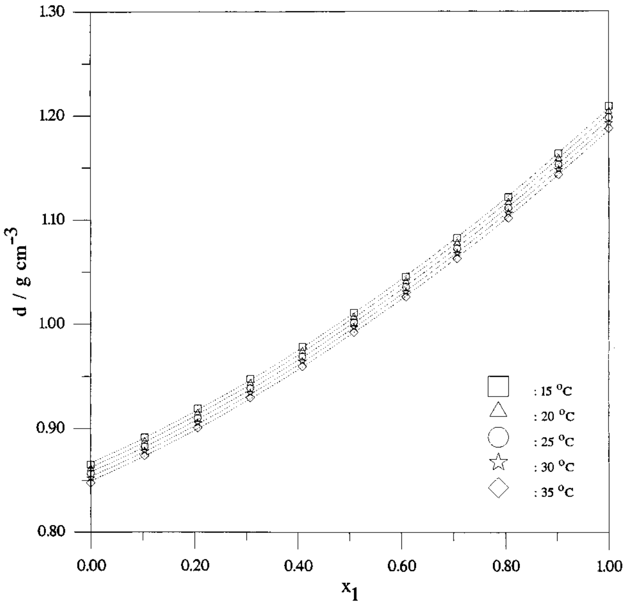

Figure 1. Variation of density *d* with the mole fraction of propylene carbonate x_1. The dotted curves are to indicate general trends only.

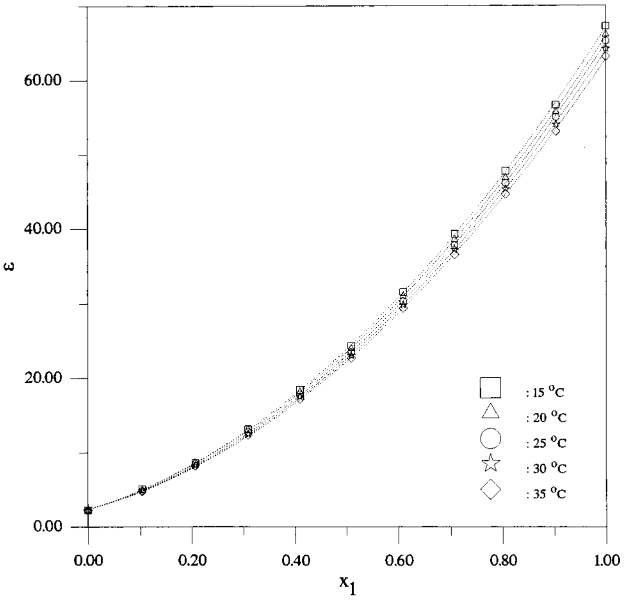

Figure 2. Variation of relative permittivity ϵ with the mole fraction of propylene carbonate x_1. The dotted curves are to indicate general trends only.

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Table 1. Densities, Relative Permittivities, and Refraction Indices of Propylene Carbonate (1) + *p*-Xylene (2) at (15, 20, 25, 30, and 35) °C

x_1	d/g cm^{-3}	ϵ	n_D	x_1	d/g cm^{-3}	ϵ	n_D
			15 °C				
0.0000	0.8653	2.28	1.4981	0.5098	1.0105	24.35	1.4660
0.1036	0.8915	5.10	1.4927	0.6094	1.0449	31.49	1.4584
0.2063	0.9189	8.61	1.4869	0.7082	1.0818	39.25	1.4503
0.3083	0.9476	13.08	1.4800	0.8062	1.1209	47.75	1.4415
0.4094	0.9781	18.39	1.4732	0.9035	1.1631	56.64	1.4327
				1.0000	1.2087	67.20	1.4232
			20 °C				
0.0000	0.8612	2.27	1.4958	0.5098	1.0060	23.95	1.4639
0.1036	0.8873	4.98	1.4904	0.6094	1.0403	30.90	1.4564
0.2063	0.9145	8.62	1.4847	0.7082	1.0771	38.46	1.4483
0.3083	0.9432	13.06	1.478	0.8062	1.1160	46.84	1.4396
0.4094	0.9737	18.14	1.4711	0.9035	1.1580	55.65	1.4306
				1.0000	1.2034	66.03	1.4214
			25 °C				
0.0000	0.8566	2.26	1.4931	0.5098	1.0011	23.46	1.4617
0.1036	0.8828	4.90	1.4878	0.6094	1.0354	30.26	1.4542
0.2063	0.9099	8.47	1.4820	0.7082	1.0720	37.74	1.4463
0.3083	0.9385	12.71	1.4756	0.8062	1.1107	46.10	1.4375
0.4094	0.9688	17.76	1.4687	0.9035	1.1524	54.95	1.4286
				1.0000	1.1978	65.16	1.4194
			30 °C				
0.0000	0.8521	2.25	1.4904	0.5098	0.9963	23.02	1.4593
0.1036	0.8782	4.88	1.4852	0.6094	1.0305	29.76	1.4519
0.2063	0.9053	8.25	1.4796	0.7082	1.0671	37.15	1.4440
0.3083	0.9338	12.46	1.4730	0.8062	1.1058	45.28	1.4354
0.4094	0.9641	17.48	1.4663	0.9035	1.1474	53.96	1.4266
				1.0000	1.1926	64.13	1.4177
			35 °C				
0.0000	0.8478	2.24	1.4878	0.5098	0.9917	22.67	1.4570
0.1036	0.8739	4.80	1.4826	0.6094	1.0258	29.30	1.4497
0.2063	0.9009	8.20	1.4771	0.7082	1.0624	36.49	1.442
0.3083	0.9294	12.31	1.4705	0.8062	1.1010	44.58	1.4335
0.4094	0.9596	17.18	1.4639	0.9035	1.1426	53.07	1.4246
				1.0000	1.1873	63.07	1.4155

Table 2. Experimental and Literature Values of Physical Properties of the Pure Liquids at 25 °C

	d/g cm^{-3}		ϵ		n_D	
	propylene carbonate	*p*-xylene	propylene carbonate	*p*-xylene	propylene carbonate	*p*-xylene
this work	1.1978	0.8566	65.16	2.26	1.4194	1.4931
Kronick and Fuoss, 1955	1.1970		65.10			
Wu and Friedman, 1966	1.1980					
Hanna and Al-Sudani, 1987	1.1989		65.04			
Payne and Theodorou, 1972			64.92			
Buep and Baron, 1988		0.85673		2.262		1.49312
Nath and Narain, 1982				2.26		1.4932
Tasioula-Margari and Demetropoulos, 1992		0.8566				

Table 3. Coefficients a_j from Equation 2 and Standard Deviation σ for Propylene Carbonate (1) + *p*-Xylene (2)

t (°C)	a_0	a_1	a_2	a_3	σ/cm^3 mol^{-1}
15	−0.781	0.201	−0.122	0.499	0.011
20	−0.848	0.138	−0.148	0.698	0.019
25	−0.937	0.039	−0.149	1.081	0.026
30	−0.976	0.033	−0.196	0.935	0.025
35	−1.025	0.072	−0.403	0.612	0.035

Table 4. Calculated Values of V^E from Equation 2, for the Used Values of Mole Fraction x_1 for Propylene Carbonate (1) + *p*-Xylene (2)

	V^E				
x_1	15 °C	20 °C	25 °C	30 °C	35 °C
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1036	−0.1175	−0.1298	−0.1486	−0.1477	−0.1522
0.2063	−0.1706	−0.1836	−0.2014	−0.2051	−0.2178
0.3083	−0.1928	−0.2051	−0.2206	−0.2282	−0.2444
0.4094	−0.1993	−0.2132	−0.2310	−0.2404	−0.2550
0.5098	−0.1942	−0.2112	−0.2340	−0.2438	−0.2558
0.6094	−0.1756	−0.1945	−0.2200	−0.2306	−0.2433
0.7082	−0.1410	−0.1582	−0.1795	−0.1920	−0.2110
0.8062	−0.0920	−0.1029	−0.1126	−0.1273	−0.1549
0.9035	−0.0380	−0.0407	−0.0379	−0.0511	−0.0792
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 5. Coefficients b_j from Equation 4 and Standard Deviation σ for Propylene Carbonate (1) + *p*-Xylene (2)

t (°C)	b_0	b_1	b_2	b_3	b_4	σ
15	−18.16	12.70	−2.76	−8.92	−6.63	0.304
20	−18.24	10.59	2.29	−6.03	−13.77	0.183
25	−18.85	10.17	2.50	−4.28	−11.52	0.160
30	−18.48	10.43	−0.86	−5.91	−7.55	0.260
35	−18.28	10.19	1.55	−5.90	−11.16	0.203

dance with National Bureau of Standards Circular 514 (Weast, 1987−1988). The uncertainty was better than 0.3%.

An Abbe refractometer (aus JENA, model G) of closed type was used for measuring the refractive indices. All values were obtained for Na D light with an error better than ±0.0002 units. The same thermostat mentioned in relative permittivity was used. The refractometer was checked with distilled water and *a*-bromonaphthalene.

Results and Discussion

The experimental results of densities, relative permittivities, and refractive indices are given in Table 1. The experimental values of the pure components at 25 °C are listed in Table 2 in comparison with literature values. As can be seen, our values are in an agreement with the values reported in the literature.

Variations of density, relative permittivity, and refractive index with the mole fraction of propylene carbonate are given in Figures 1−3, respectively. On increasing the mole fraction of propylene carbonate, density and relative permittivity values increase, whereas refractive index values decrease. This is the same for the five temperatures where

Table 6. Calculated Values of $\Delta\epsilon$ from Equation 4, for the Used Values of Volume Fraction ϕ_1 for Propylene Carbonate (1) + *p*-Xylene (2)

15 °C		20 °C		25 °C		30 °C		35 °C	
ϕ_1	$\Delta\epsilon$	ϕ_1	$\Delta\epsilon$	ϕ_1	$\Delta\epsilon$	ϕ_1	$\Delta\epsilon$	ϕ_1	$\Delta\epsilon$
0.0000	0.000	0.0000	0.000	0.0000	0.000	0.0000	0.000	0.0000	0.000
0.0737	−1.977	0.0737	−1.989	0.0736	−1.987	0.0736	−1.930	0.0735	−1.913
0.1518	−3.462	0.1518	−3.309	0.1517	−3.344	0.1516	−3.336	0.1515	−3.247
0.2348	−4.468	0.2347	−4.204	0.2346	−4.277	0.2344	−4.303	0.2343	−4.173
0.3231	−4.966	0.3230	−4.734	0.3228	−4.838	0.3226	−4.839	0.3225	−4.723
0.4172	−4.937	0.4171	−4.842	0.4169	−4.974	0.4167	−4.915	0.4166	−4.841
0.5178	−4.422	0.5177	−4.460	0.5175	−4.617	0.5173	−4.525	0.5172	−4.477
0.6255	−3.587	0.6254	−3.652	0.6253	−3.809	0.6251	−3.761	0.6249	−3.697
0.7412	−2.693	0.7411	−2.690	0.7410	−2.777	0.7408	−2.827	0.7407	−2.741
0.8656	−1.830	0.8656	−1.811	0.8655	−1.751	0.8654	−1.838	0.8653	−1.805
1.0000	0.000	1.0000	0.000	1.0000	0.000	1.0000	0.000	1.0000	0.000

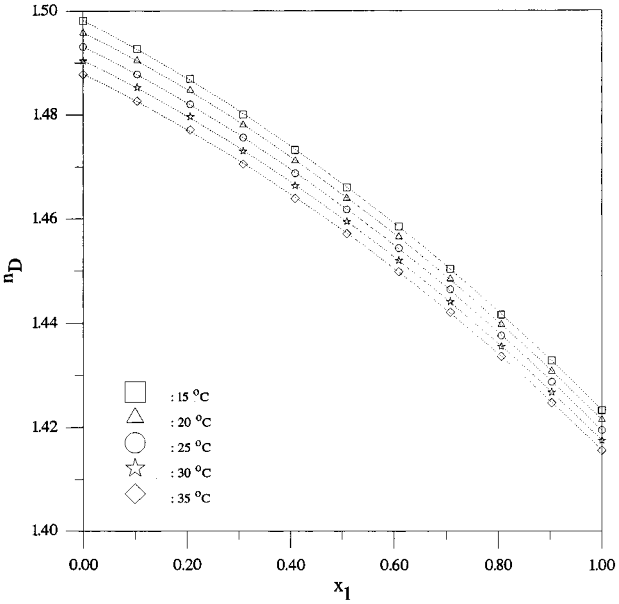

Figure 3. Variation of refractive index n_D with the mole fraction of propylene carbonate x_1. The dotted curves are to indicate general trends only.

Table 7. Coefficients c_j from Equation 6 and Standard Deviation σ for Propylene Carbonate (1) + *p*-Xylene (2)

t (°C)	c_0	c_1	c_2	σ/cm^3 mol^{-1}
15	−5.634	1.027	−0.088	0.042
20	−5.646	0.994	−0.210	0.046
25	−5.650	1.045	−0.246	0.030
30	−5.670	1.031	−0.168	0.044
35	−5.705	1.041	−0.254	0.051

measurements were made. On increasing the temperature, all the above quantities decrease.

Excess volume V^E was determined from density measurements using the equation

$$V^E = M_1x_1\left(\frac{1}{d} - \frac{1}{d_1}\right) + M_2x_2\left(\frac{1}{d} - \frac{1}{d_2}\right) \quad (1)$$

where M_i and x_i are respectively the molar mass and the mole fraction of the ith component, d is the density of the mixture, and d_i is the density of the ith pure component. The results where fitted through least squares to a Redlich−Kister type equation (Redlich and Kister, 1948)

$$V^E = x_1x_2\sum_{j=0} a_j(x_1 - x_2)^j \quad (2)$$

The values of coefficients a_j and the standard deviations are summarized in Table 3. The calculated values of V^E from eq 2 are given in Table 4.

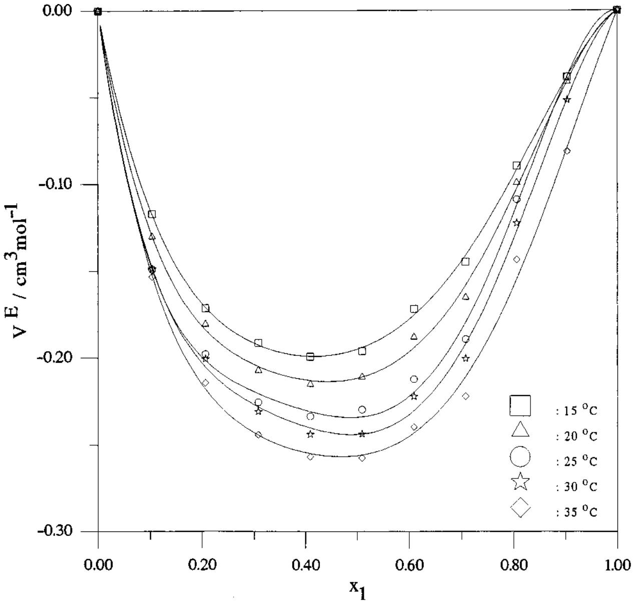

Figure 4. Plot of V^E against mole fraction of propylene carbonate x_1. Curves are least squares representations by eq 2.

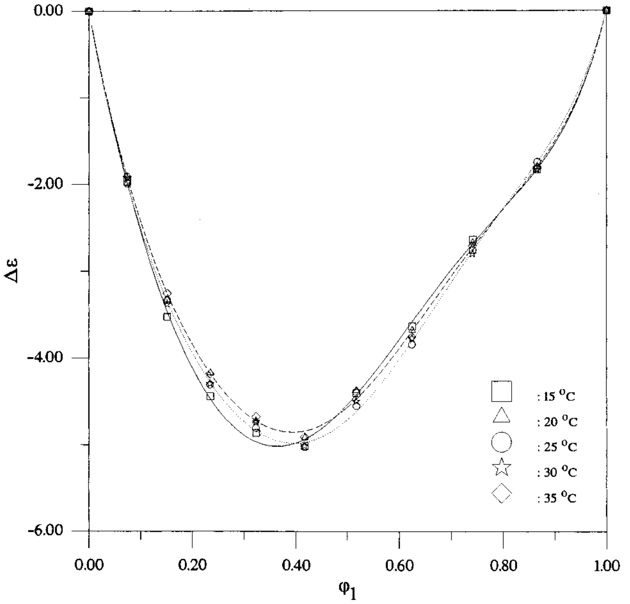

Figure 5. Plot of $\Delta\epsilon$ against volume fraction of propylene carbonate ϕ_1: (—) 15 °C; (···) 25 °C; (- - -) 35 °C. Curves are least squares representations by eq 4.

The deviation in relative permittivity $\Delta\epsilon$ was calculated from the equation

$$\Delta\epsilon = \epsilon - (\phi_1\epsilon_1 + \phi_2\epsilon_2) \quad (3)$$

Table 8. Calculated Values of Δ[R] from Equation 6, for the Used Values of Volume Fraction ϕ_1 for Propylene Carbonate (1) + *p*-Xylene (2)

15 °C		20 °C		25 °C		30 °C		35 °C	
ϕ_1	Δ[R]	ϕ_1	Δ[R]	ϕ_1	Δ[R]	ϕ_1	Δ[R]	ϕ_1	Δ[R]
0.0000	0.000	0.0000	0.000	0.0000	0.000	0.0000	0.000	0.0000	0.000
0.0737	−0.449	0.0737	−0.453	0.0736	−0.458	0.0736	−0.455	0.0735	−0.462
0.1518	−0.823	0.1518	−0.829	0.1517	−0.836	0.1516	−0.832	0.1515	−0.842
0.2348	−1.115	0.2347	−1.120	0.2346	−1.127	0.2344	−1.124	0.2343	−1.136
0.3231	−1.314	0.3230	−1.317	0.3228	−1.323	0.3226	−1.324	0.3225	−1.334
0.4172	−1.412	0.4171	−1.414	0.4169	−1.417	0.4167	−1.421	0.4166	−1.430
0.5178	−1.398	0.5177	−1.401	0.5175	−1.402	0.5173	−1.407	0.5172	−1.416
0.6255	−1.261	0.6254	−1.267	0.6253	−1.266	0.6251	−1.271	0.6249	−1.280
0.7412	−0.990	0.7411	−1.001	0.7410	−0.999	0.7408	−1.001	0.7407	−1.011
0.8656	−0.573	0.8656	−0.585	0.8655	−0.584	0.8654	−0.583	0.8653	−0.592
1.0000	0.000	1.0000	0.000	1.0000	0.000	1.0000	0.000	1.0000	0.000

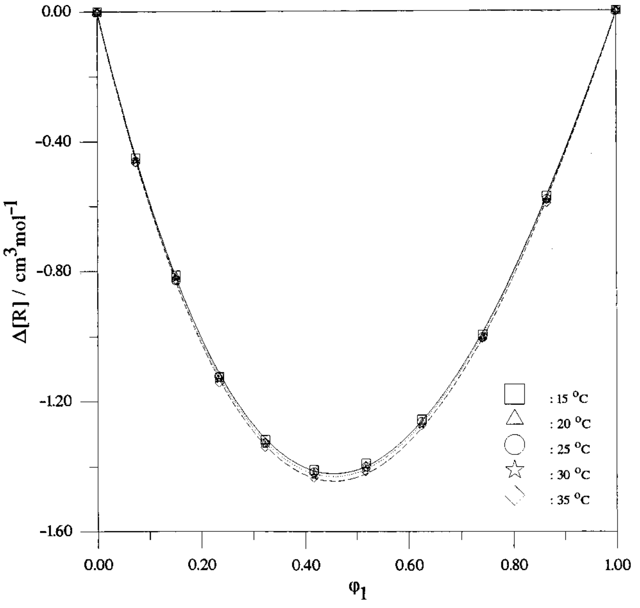

Figure 6. Plot of Δ[R] against volume fraction of propylene carbonate ϕ_1: (—) 15 °C; (···) 25 °C; (- - -) 35 °C. Curves are least square representations by eq 6.

where ϵ_i is the relative permittivity of the *i*th pure component, ϵ is the relative permittivity of the mixture, and ϕ_i is the volume fraction of the *i*th component, defined by $\phi_i = x_iV_i/\sum_{i=1}^{2}x_iV_i$. The values of the deviations were fitted to the equation

$$\Delta\epsilon = \phi_1\phi_2\sum_{j=0} b_j(\phi_1 - \phi_2)^j \qquad (4)$$

The values of coefficients b_j and the standard deviations are given in Table 5, whereas the calculated values of Δϵ are in Table 6.

The quantity Δ[R], which gives the deviation in molar refractivity with the volume fraction, was calculated from the equation based on the Lorentz−Lorentz mixing rule (Lorentz, 1909; Áminabhavi et al., 1993)

$$\Delta[R] = [R] - (\phi_1[R]_1 + \phi_2[R]_2) \qquad (5)$$

where [R] is the molar refractivity of the mixture and $[R]_i$ is the molar refractivity of the *i*th pure component. Molar refractivity is defined by $[R] = [(n_D^2 - 1)/(n_D^2 + 2)]V$, where n_D is the refractive index and *V* is the molar volume. The values of the Δ[R] were also fitted by the least squares method to the Redlich−Kister type equation

$$\Delta[R] = \phi_1\phi_2\sum_{j=0} c_j(\phi_1 - \phi_2)^j \qquad (6)$$

Values of coefficients c_j and standard deviations are summarized in Table 7, and calculated values of Δ[R] are in Table 8.

Variation of excess volume with the mole fraction of propylene carbonate is given in Figure 4. The deviations from ideality are negative, with a minimum at about $x_1 \approx 0.5$, at all temperatures. On increasing the temperature, the minimum becomes more negative. This has been observed in many systems (Janelli et al., 1983; Lopez et al., 1983; Moumouzias et al., 1991; Moumouzias and Ritzoulis 1992). The negative values of V^E can be attributed to the different sizes of propylene carbonate and *p*-xylene molecules and to the specific interactions due to a dipole-induced dipole effect (Prigogine, 1957; Palepu, 1985; Fort and Moore, 1965).

The variation of Δϵ with the volume fraction of propylene carbonate is shown in Figure 5. Δϵ is found to be negative with a minimum at about $\phi_1 \approx 0.45$, without considerable changes over the temperature range studied. The negative values of deviations in permittivity occur in mixtures of high relative permittivity liquids with nonpolar liquids (Payne and Theodorou, 1972).

In Figure 6, the variation of Δ[R] with the volume fraction of propylene carbonate is shown. Values are negative here too, with a minimum at about $\phi_1 \approx 0.45$. The temperature contribution was not found to be very important.

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