Relative Permittivities and Refractive Indices of Propylene Carbonate + Toluene Mixtures from 283.15 K to 313.15 K

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The relative permittivities, ϵ_r, and refractive indices, n_D, have been measured over the whole composition range for binary mixture propylene carbonate + toluene at temperatures from 283.15 K to 313.15 K. The relative permittivity of the mixture increased monotonically by addition of propylene carbonate. Calculated deviations in relative permittivity, $\Delta\epsilon_r$, were always negative showing a minimum. From the values of ϵ_r and n_D, the molar polarizability, P_m, has been calculated from the Kirkwood−Fröhlich equation and the deviation in molar polarizability, ΔP_m, has been estimated. Molar refractivity, R_m, was also calculated.

Introduction

Propylene carbonate is an aprotic solvent and one of the most popular ones used for chemical and electrochemical applications and studies. Binary mixtures which contain propylene carbonate and other organic solvents, especially aprotic ones, also have great technological and theoretical interest (Gabano, 1983).

This paper is part of an on-going study on the physical and thermophysical properties of binary liquid mixtures where one or both components are dipolar-aprotic solvents. We present here the experimental results of relative permittivity, ϵ_r, and refractive index, n_D, of the mixture propylene carbonate (1) + toluene (2) over the whole composition range at temperatures ranging from 283.15 K to 313.15 K. The molar refractivity and the molar polarizability were calculated from the values of relative permittivity, refractive index, and density, and the deviation in molar polarizability, ΔP_m, was estimated. The deviation in relative permittivity, $\Delta\epsilon_r$, was calculated as well.

Experimental Section

Propylene carbonate (Merck, zur synthese >99%) was dried with 5A molecular sieves and fractionally distilled under vacuum. The middle fraction was collected. Toluene (Merck, extra pure >99.5%) was distilled twice, and the middle fraction was collected and used.

The relative permittivities were measured with a dipolmeter (WTW, type DM 01) with a frequency of 2 MHz. The three measuring cells used were previously calibrated with carbon tetrachloride, benzene, chlorobenzene, 1,2-dichloroethane, benzyl alcohol, nitrobenzene, and water in accordance with the National Bureau of Standards Circular 514 (Weast, 1987−1988). The cells were thermostated to ±0.005 K by a YSI (model 72) thermostat. The uncertainty in ϵ_r was better than 0.3%.

The refractive indices were measured by means of an Abbe refractometer (aus JENA, model G), which was thermostated to ±0.005 K using the same thermostat mentioned earlier for permittivity measurements. Values were obtained using sodium light (D). The refractometer was calibrated with distilled water and a-bromonaphthalene. The error in n_D measurements was better than ±0.0002 units.

The densities of the mixtures at temperatures 283.15 K and 313.15 K were measured with an Anton-Paar DMA 60/602 vibrating tube densimeter which was calibrated with air and double-distilled water and thermostated by a Haake F3-K Digital thermostat with a stability of ±0.02 °C. The accuracy in density values was higher than $\pm 5 \times 10^{-5}$ g cm^{-3}.

All solutions were prepared by mass, with a Shimatzu, AEG-220 analytical balance with four decimals. The atomic masses were taken from the atomic mass table of IUPAC (IUPAC, 1986). The error in the mole fraction was estimated to be lower than ±0.00003.

Table 1. Literature Values of Densities (ρ/g cm^{-3}), Relative Permittivities (ϵ_r), and Refraction Indices (n_D) in Propylene Carbonate (1) and Toluene (2)

		288.15 K	298.15 K	308.15 K
propylene carbonate (1)	ρ	1.2087[a]	1.1978[a]	1.1873[a]
		1.2094[b]	1.1995[b]	1.1892[b]
		1.2100[c]	1.1970[d]	1.1872[c]
			1.1980[e]	
	ϵ_r	67.20[a]	65.16[a]	63.07[a]
		67.60[b]	65.10[b]	62.70[b]
		67.41[f]	65.10[d]	62.58[f]
			64.92[f]	
	n_D	1.4232[a]	1.4194[a]	1.4155[a]
toluene (2)	ρ	0.8712[a]	0.8621[a]	0.8526[a]
		0.8716[g]	0.8623[g]	0.8527[g]
			0.8621[i]	
			0.8622[j]	
	ϵ_r	2.39[a]	2.37[a]	2.35[a]
		2.40[g]	2.375[j]	2.355[g]
			2.38[g]	
	n_D	1.4992[a]	1.4938[a]	1.4883[a]
			1.49405[j]	1.48802[j]

[a] This work. [b] Salomon (1969). [c] Simeral and Amey (1970). [d] Kronick and Fuoss (1955). [e] Wu and Friedman (1966). [f] Payne and Theodorou (1972). [g] Ritzoulis et al. (1986). [i] Mamagakis and Panayiotou (1989). [j] Buep and Baron (1988).

Results and Discussion

The experimental values for pure liquids are reported in Table 1 with those given in the literature for comparison.

The experimental values for the density, ρ, of the binary mixture propylene carbonate (1) + toluene (2) at temperatures 283.15 K and 313.15 K through the whole mole fraction range are given in Table 2. Density values from 288.15 K to 308.15 K are reported in a previous paper (Moumouzias and Ritzoulis, 1992).

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Table 2. Density (ρ) for Propylene Carbonate (1) + Toluene (2) Mixtures

	ρ/(g cm^{-3})			ρ/(g cm^{-3})	
x_1	283.15 K	313.15 K	x_1	283.15 K	313.15 K
0.0000	0.8760	0.8481	0.5752	1.0565	1.0276
0.0453	0.8888	0.8612	0.6780	1.0930	1.0638
0.0911	0.9025	0.8747	0.7831	1.1313	1.1012
0.1841	0.9296	0.9022	0.8904	1.1716	1.1405
0.2789	0.9580	0.9307	0.9449	1.1927	1.1608
0.3757	0.9892	0.9615	1.0000	1.2141	1.1821
0.4744	1.0219	0.9935			

Table 3. Relative Permittivity (ϵ_r) and Refractive Index (n_D) Data for Propylene Carbonate (1) + Toluene (2) Mixtures

	T/K						
x_1	283.15	288.15	293.15	298.15	303.15	308.15	313.15
				ϵ_r			
0.0000	2.40	2.39	2.38	2.37	2.36	2.35	2.34
0.0453	3.63	3.62	3.61	3.60	3.60	3.58	3.57
0.0911	5.30	5.25	5.17	5.10	5.04	5.00	4.92
0.1841	9.11	8.96	8.86	8.70	8.52	8.43	8.27
0.2789	13.67	13.48	13.21	13.00	12.76	12.61	12.36
0.3757	18.72	18.40	18.17	17.68	17.38	16.97	16.61
0.4744	25.14	24.59	24.25	23.74	23.18	22.73	22.26
0.5752	32.24	31.62	31.08	30.44	29.72	29.27	28.61
0.6780	40.02	39.23	38.63	37.73	36.94	36.32	35.52
0.7831	48.53	47.58	46.85	45.84	44.91	44.08	43.17
0.8904	57.93	56.95	55.97	54.88	53.77	53.04	51.92
0.9449	62.86	61.90	60.83	59.99	58.91	57.97	56.98
1.0000	67.96	67.20	66.03	65.16	64.13	63.07	61.94
				n_D			
0.0000	1.5020	1.4992	1.4967	1.4938	1.4913	1.4883	1.4857
0.0453	1.4994	1.4966	1.4943	1.4914	1.4889	1.486	1.4835
0.0911	1.4966	1.4938	1.4916	1.4886	1.4862	1.4834	1.4809
0.1841	1.4902	1.4875	1.4854	1.4825	1.4804	1.4774	1.4751
0.2789	1.4829	1.4808	1.4785	1.4761	1.4741	1.4719	1.4696
0.3757	1.4764	1.4740	1.4720	1.4692	1.4673	1.4649	1.4626
0.4744	1.4679	1.4659	1.4637	1.4622	1.4604	1.4577	1.4561
0.5752	1.4609	1.4591	1.4563	1.4536	1.4525	1.4501	1.4478
0.6780	1.4527	1.4509	1.4481	1.4456	1.4442	1.4419	1.4396
0.7831	1.4432	1.4412	1.4399	1.4364	1.4347	1.4338	1.4312
0.8904	1.4343	1.4325	1.4304	1.4283	1.4263	1.4249	1.4227
0.9449	1.4297	1.4279	1.4259	1.4236	1.4217	1.4202	1.418
1.0000	1.4252	1.4232	1.4213	1.4194	1.4174	1.4155	1.4133

Table 4. Coefficients a_i of Eq 1 and Standard Deviations σ for the Binary Mixture Propylene Carbonate (1) + Toluene (2)

	T/K						
	283.15	288.15	293.15	298.15	303.15	308.15	313.15
a_0	2.38	2.35	2.34	2.32	2.30	2.32	2.31
a_1	27.51	27.98	27.34	27.50	27.40	26.61	26.27
a_2	47.80	42.96	42.94	38.58	35.53	35.30	33.16
a_3	−9.72	−6.15	−6.67	−3.32	−1.22	−1.22	0.16
σ	0.09	0.09	0.07	0.11	0.11	0.12	0.13

The experimental values of relative permittivity, ϵ_r, of the mixture at various mole fractions and at the given temperatures are listed in Table 3, as well as those of the refractive index, n_D. The variations of the relative permittivity and refractive index with the mole fraction of propylene carbonate are shown in Figures 1 and 2 respectively.

The following equations

$$\epsilon_r = \sum_{j=0} a_j x_1^j \quad (1)$$

and

$$n_D = \sum_{j=0} b_j x_1^j \quad (2)$$

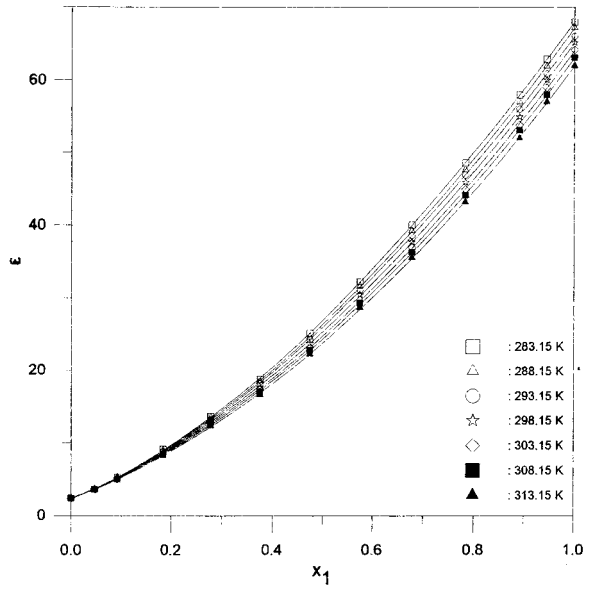

Figure 1. Variation of relative permittivity, ϵ_r, with the mole fraction of propylene carbonate, x_1. Curves are drawn according to eq 1.

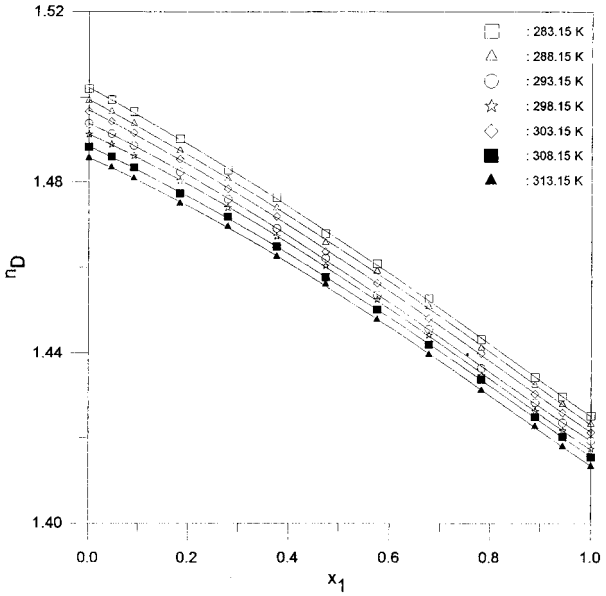

Figure 2. Variation of refractive index, n_D, with the mole fraction of propylene carbonate, x_1. Curves are drawn according to eq 2.

Table 5. Coefficients b_i of Eq 2 and Standard Deviations σ for the Binary Mixture Propylene Carbonate (1) + Toluene (2)

	T/K						
	283.15	288.15	293.15	298.15	303.15	308.15	313.15
b_0	1.502	1.499	1.497	1.494	1.491	1.488	1.486
b_1	−0.063	−0.061	−0.060	−0.054	−0.052	−0.053	−0.050
b_2	−0.020	−0.019	−0.024	−0.036	−0.035	−0.028	−0.035
b_3	0.006	0.004	0.008	0.016	0.013	0.008	0.012
σ (10^4)	3.27	3.13	2.57	2.35	2.50	1.68	2.24

were used in order to give smoothing values for ϵ_r and n_D respectively. The ajustable coefficients a_j and b_j were obtained by a regression analysis based on the least-squares method and are summarized in Tables 4 and 5.

The deviations in relative permittivity of the mixture were calculated from the common expression (Ritzoulis et al., 1986; Seshadri and Subrahmanyam, 1990; Ruostesuo and Liias-Lepisto, 1991; Corradini et al., 1992; Moumouzias

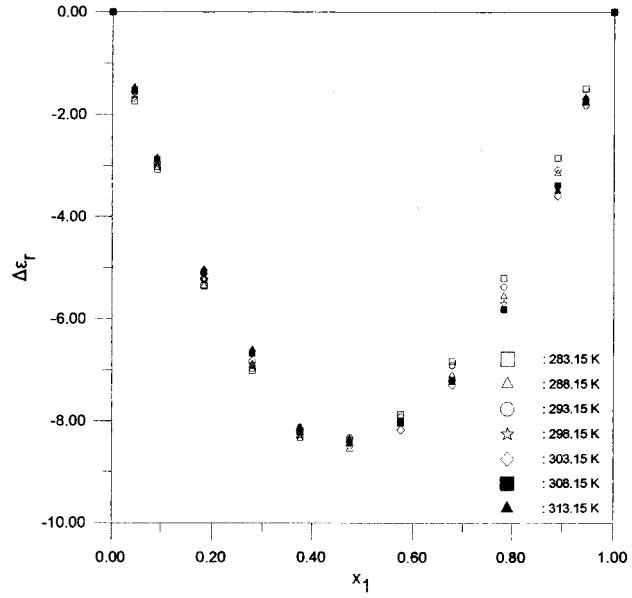

Figure 3. Plot of $\Delta\epsilon_r$ against mole fraction of propylene carbonate, x_1.

Table 6. Calculated Values of Molar Refractivity, R_m/(cm^3 mol^{-1}), for Propylene Carbonate (1) + Toluene (2) Mixtures

	T/K						
x_1	283.15	288.15	293.15	298.15	303.15	308.15	313.15
	R_m						
0.0000	31.041	31.064	31.093	31.104	31.140	31.152	31.176
0.0453	30.609	30.625	30.657	30.661	30.693	30.707	30.732
0.0911	30.148	30.161	30.198	30.190	30.223	30.243	30.267
0.1841	29.237	29.247	29.279	29.273	29.318	29.309	29.329
0.2789	28.291	28.318	28.336	28.337	28.382	28.402	28.434
0.3757	27.358	27.370	27.399	27.382	27.425	27.431	27.444
0.4744	26.344	26.368	26.388	26.427	26.469	26.462	26.507
0.5752	25.413	25.443	25.430	25.407	25.476	25.482	25.485
0.6780	24.440	24.467	24.448	24.434	24.483	24.491	24.480
0.7831	23.427	23.439	23.488	23.425	23.455	23.521	23.500
0.8904	22.463	22.484	22.489	22.490	22.501	22.541	22.537
0.9449	21.979	21.997	22.005	22.000	22.012	22.045	22.044
1.0000	21.510	21.517	21.527	21.542	21.545	21.555	21.549

Table 7. Calculated Values of Molar Polarizability, P_m (cm^3 mol^{-1}), for Propylene Carbonate (1) + Toluene (2) Mixtures

	T/K						
x_1	283.15	288.15	293.15	298.15	303.15	308.15	313.15
	P_m						
0.0000	4.95	4.92	4.86	4.84	4.78	4.77	4.72
0.0453	41.92	42.17	42.17	42.36	42.68	42.66	42.83
0.0911	84.95	84.37	82.76	81.56	80.74	80.42	78.91
0.1841	173.72	171.20	169.83	166.96	163.78	162.63	159.70
0.2789	272.85	269.90	265.38	261.77	257.81	255.60	251.26
0.3757	377.00	371.92	368.71	359.71	354.96	347.60	341.31
0.4744	504.79	495.55	490.92	481.97	472.37	465.04	457.14
0.5752	640.30	630.27	622.22	611.59	599.41	592.89	581.63
0.6780	782.33	769.88	761.29	746.36	733.83	724.69	711.05
0.7831	931.39	916.84	906.54	890.51	876.08	863.49	848.94
0.8904	1089.3	1075.4	1061.5	1044.9	1028.1	1018.5	1001.0
0.9449	1169.2	1156.3	1141.1	1130.2	1114.6	1101.6	1087.5
1.0000	1250.4	1241.7	1225.2	1214.5	1200.2	1185.4	1169.0

et al., 1991)

$$\Delta\epsilon_r = \epsilon - (x_1\epsilon_1 + x_2\epsilon_2) \tag{3}$$

Many authors prefer to use the volume fraction rather than the mole fraction (Buep and Barón, 1988; Janelli et al., 1983). Figure 3 shows the variation of $\Delta\epsilon_r$ when x_1 is varied over the entire composition range from 283.15 K to 313.15 K.

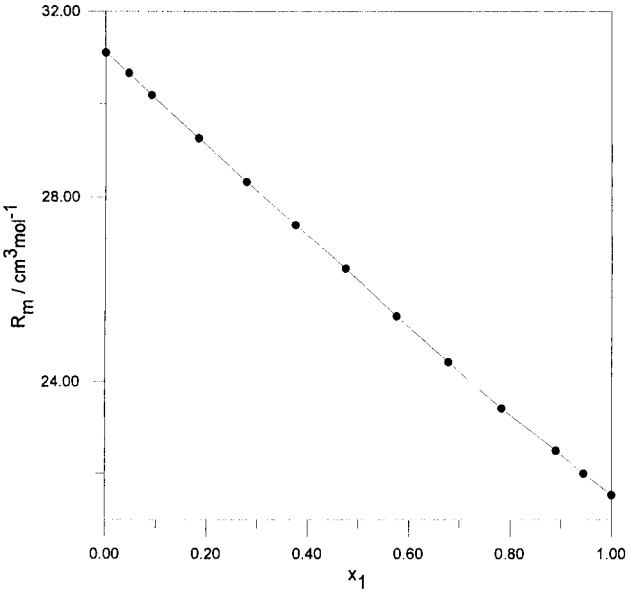

Figure 4. Variation of molar refractivity, R_m, with the mole fraction of propylene carbonate, x_1, at 298.15 K. Curve drawn manually.

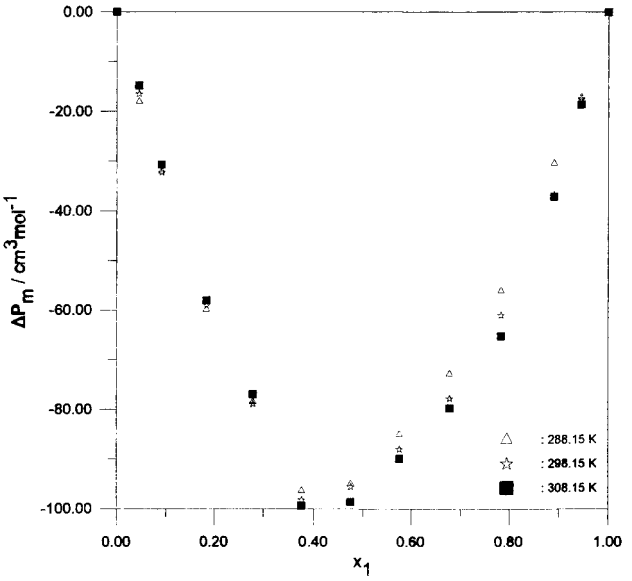

Figure 5. Plot of ΔP_m against mole fraction of propylene carbonate, x_1.

The molar refractivity, R_m, defined by the Lorentz–Lorentz equation

$$R_m = \frac{n_D^2 - 1}{n_D^2 + 2}\frac{M}{\rho} \tag{4}$$

was calculated, and the values are given in Table 6. In eq 4

$$M = M_1x_1 + M_2x_2$$

where M_1 and M_2 are the molar masses of the pure substances and ρ the density of the mixture. Variation of R_m with the mole fraction of propylene carbonate is given in Figure 4.

The relative permittivity, ϵ_r, is related to the polarizability, P_m, by the Kirkwood−Fröhlich equation

$$P_m = \frac{(\epsilon_r - n_D^2)(2\epsilon_r + n_D^2)}{9\epsilon_r} V_m \quad (5)$$

where V_m is the molar volume of the mixture. The values of P_m are given in Table 7.

The deviation in polarizability, ΔP_m, is given by

$$\Delta P_m = P_m - (x_1 P_{m,1} + x_2 P_{m,2}) \quad (6)$$

where $P_{m,i}$ refer to the polarizability of the pure component. The variation of ΔP_m in terms of mole fraction of propylene carbonate x_1 at 288.15 K, 298.15 K, and 308.15 K is shown in Figure 5.

The $\Delta\epsilon_r$ values are negative over the entire composition range. The curve $\Delta\epsilon_r$ versus x_1 presents a minimum at mole fraction of propylene carbonate $x_1 \approx 0.5$. The dependance of ΔP_m on the mole fraction of propylene carbonate, x_1, is always negative too, showing the same trend as $\Delta\epsilon_r$. The curve ΔP_m versus x_1 shows a minimum at $x_1 = 0.4$. The influence of temperature is perceptible on the area of mole fraction of propylene carbonate between $x_1 = 0.4$ and $x_1 = 1.0$, where ΔP_m becomes more negative as the temperature increases.

Literature Cited

Buep, A. H.; Barón, M. Dielectric Properties of Binary Systems. 7. Carbon Tetrachloride with Benzene, with Toluene, and with *p*-Xylene at 298.15 and 308.15 K. *J. Phys. Chem.* **1988**, *92*, 840−843.

Corradini, F.; Marcheselli, L.; Tassi, L.; Tosi, G. Static Dielectric Constants of the *N*,*N*-Dimethylformamide/2-Methoxyethanol Solvent System at Various Temperatures. *Can. J. Chem.* **1992**, *70*, 2895−2899.

Gabano, J.-P., Ed. *Lithium Batteries*; Academic Press: New York, 1983.

IUPAC. *Pure Appl. Chem.* **1986**, *58*, 1677.

Jannelli, L; Lopez, A.; Salello, S. Excess Volumes and Dielectric Constants of Benzonitrile + Nitrobenzene and Acetonitrile + Nitrobenzene Systems. *J. Chem. Eng. Data* **1983**, *28*, 169−173.

Kronick, P. L.; Fuoss, R. M. Quaternization Kinetics. II. Pyridine and 4- Picoline in Propylene Carbonate. *J. Am. Chem. Soc.* **1955**, *77*, 6114.

Mamagakis, N.; Panayiotou, C. Excess Volume and Dynamic Viscosity of Ternary Liquid Mixtures. *Z. Phys. Chem., Neue Folge* **1989**, *162*, 57−72.

Moumouzias, G; Ritzoulis, G. Viscosities and Densities for Propylene Carbonate + Toluene at 15, 20, 25, 30, and 35 °C. *J. Chem. Eng. Data* **1992**, *37*, 482−483.

Moumouzias, G; Panopoulos, D.; Ritzoulis, G. Excess Properties of the Binary Liquid System Propylene Carbonate + Acetonitrile. *J Chem. Eng. Data* **1991**, *36*, 20−23.

Payne, R.; Theodorou, I. Dielectric Properties and Relaxation in Ethylene Carbonate and Propylene Carbonate. *J. Phys. Chem.* **1972**, *76*, 2892−2900.

Ritzoulis, G.; Papadopoulos, N.; Jannakoudakis, D. Densities, Viscosities, and Dielectric Constants of Acetonitrile + Toluene at 15, 25, and 35 °C. *J. Chem. Eng. Data* **1986**, *31*, 146−148.

Ruostesuo P.; Liias-Lepisto, R. Thermodynamic and Spectroscopic Properties of Phosphorus Compounds. Part 2. Excess Volumes and Excess Dielectric Properties of Binary Mixtures of Trimethylphosphate with Dichloromethane and 1,2-Dichloroethane. *Thermochim. Acta* **1991**, *178*, 135−142.

Salomon, M. Thermodynamics of Lithium Chloride and Lithium Bromide in Propylene Carbonate. *J. Phys. Chem.* **1969**, *73*, 3299−3306.

Seshadri, A. T.; Subrahmanyam, B.; Excess Compressibility and Excess Dielectric Constant for a Morpholine-*n*-Butyl Alcohol Liquid Mixture. *J. Phys.: Condens. Matter* **1990**, *2*, 7353−7360.

Simeral, L.; Amey, R. Dielectric Properties of Liquid Propylene Carbonate. *J. Phys. Chem.* **1970**, *74*, 1443−1446.

Weast, R., Ed. *Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1987−1988 (from National Bureau of Standards Circular 514).

Wu, Y.; Friedman, H. L. Heats of Solution of SomeTrifluoroacetates, Tetraphenylborate, Iodides, and Perchlorates in Water and in Propylene Carbonate and the Relative Enthalpies of Solvation of the Alkali Metal Ions in Propylene Carbonate. *J. Phys. Chem.* **1966**, *70*, 501−509.

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