J. Chem. Eng. Data **1996,** *41,* 1473−1476

Viscosities and Excess Molar Volumes of Binary Mixtures of Propylene Carbonate with Tetrahydrofuran and Methanol at Different Temperatures

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Densities and viscosities of the binary mixtures of propylene carbonate with methanol and tetrahydrofuran have been measured at (298.15, 308.15, and 318.15) K. The excess molar volumes and the deviations of the viscosity of the mixture from the ideal mole fraction rule have been calculated from these data. The computed results have been fitted to the Redlich−Kister polynomial relation to estimate the regression coefficients and standard errors for these systems.

Introduction

Recently, there has been increased interest in the thermodynamic and transport properties of organic binary liquid mixtures and some of these have been extensively used to obtain information on the intermolecular interactions in these systems. The potentiality of propylene carbonate (PC) as a solvent for a variety of applications particularly in high-energy batteries has been widely stressed (Jasinski, 1967a,b). Solvents like 2-methoxyethanol, 1,2-dimethoxyethane (DME), tetrahydrofuran, and methanol find a wide range of applications of technological importance (Grast, 1969; Matsuda and Satake, 1980). However, there have been relatively few studies on the binary systems of propylene carbonate with other nonaqueous solvents (Ritzoulis, 1989; Moumouzias et al., 1991).

Recently, we have reported the viscosities and excess molar volumes of binary mixtures of propylene carbonate with 1,2-dimethoxyethane and 2-methoxyethanol (Muhuri and Hazra, 1994, 1995). In the present study, the excess molar volumes (V^E) and viscosities (η) of the binary mixtures of propylene carbonate with methanol and tetrahydrofuran have been determined over the entire composition range and at three different temperatures. Attempts have been made to explain the behavior of the liquid mixtures from these properties. The McAllister equation has also been used to calculate the interaction parameters from the kinematic viscosity data.

Experimental Section

Propylene carbonate (Merck > 99% pure) was dried over freshly ignited quicklime for several hours and then distilled three times under reduced pressure in a nitrogen atmosphere, the middle fraction being taken each time. The purified solvent had a density of 1.198 83 g·cm^{-3} and viscosity of 2.471 mPa·s at 298.15 K; these values are in good agreement with the literature values which are 1.1993 g·cm^{-3} and 2.480 mPa·s, respectively (Jansen and Yeager, 1973, 1974).

Methanol (E. Merck, Uvasol grade) was dried over 3A molecular sieves and distilled fractionally. The middle fraction was taken and further distilled. Physical properties of purified methanol (density = 0.786 63 g·cm^{-3} and viscosity = 0.5437 mPa·s at 298.15 K) agreed well with the literature values: 0.7866 g·cm^{-3} and 0.5445 mPa·s, respectively (Covington and Dickinson, 1973).

Tetrahydrofuran (E. Merck) was kept over KOH, refluxed for 24 h, and distilled over $LiAlH_4$. The density (0.880 72 g·cm^{-3}) and viscosity (0.4630 mPa·s) at 298.15 K of the purified sample are in good conformity with the literature values (Covington and Dickinson, 1973) which are 0.8811 g·cm^{-3} and 0.460 mPa·s, respectively.

The densities, ρ, were measured with an Ostwald−Sprengel-type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at (298.15, 308.15, and 318.15) K with doubly distilled water and benzene. The temperature of the bath was controlled to ±0.01 K. The reproducibility of density measurements was $\pm 3 \times 10^{-5}$ g·cm^{-3}.

The kinematic viscosities, ν, were measured by means of a suspended level Ubbelohde viscometer. The time of efflux was measured with a stopwatch to ±0.1 s. The viscometer was kept in a vertical position in a water thermostat controlled to ±0.01 K. The absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge. The efflux time for water at 298.15 K was about 540 s. The kinematic viscosity (ν) and the absolute viscosity (η) are given by the following equations:

$$\nu = Ct - K/t \tag{1}$$

$$\eta = \nu\rho \tag{2}$$

where t is the efflux time, ρ is the density, and C and K are the characteristic constants of the viscometer. The values of the constants C and K, determined by using the density and viscosity values of water and benzene (Saha et al., 1995) were found to be 1.648×10^{-5} cm^2·s^{-2} and −0.023 316 47 cm^2, respectively. The estimated error of the viscosity measurements was ±0.2%.

In all cases the experiments were performed at least in five replicates for each composition and at each temperature, and the results were averaged.

Results

The experimental results of densities and viscosities at various mole fractions and at three temperatures are reported in Table 1. Graphical representations of η as functions of the mole fraction of component 2 are given in Figures 1 and 2.

The kinematic viscosity data have been analyzed by means of the McAllister equation as described earlier

S0021-9568(96)00196-3 CCC: $12.00

Table 1. Experimental Density (ρ), Absolute Viscosity (η), Excess Molar Volume (V^E), Viscosity Deviation ($\Delta\eta$), and the McAllister Interaction Parameters (ν_{ij}) for the Binary Mixtures of Propylene Carbonate with Tetrahydrofuran and Methanol at 298.15, 308.15, and 318.15 K

x_2	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}	$\Delta\eta$/mPa·s	x_2	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}	$\Delta\eta$/mPa·s
Propylene Carbonate (1) + Tetrahydrofuran (2)									
T = 298.15 K									
0.000	1.198 83	2.4711	0.000	0.000	0.6094	1.012 21	0.8417	0.349	0.406
0.0524	1.183 73	2.2270	0.069	0.139	0.6479	0.999 23	0.7836	0.302	0.386
0.1036	1.168 99	2.0225	0.143	0.241	0.7082	0.979 00	0.7171	0.241	0.332
0.1429	1.157 43	1.8695	0.186	0.315	0.7635	0.960 36	0.6549	0.183	0.283
0.2064	1.138 88	1.6736	0.273	0.383	0.8062	0.946 20	0.6195	0.161	0.233
0.2431	1.127 77	1.5666	0.299	0.416	0.8388	0.934 89	0.5831	0.104	0.204
0.3083	1.107 86	1.3932	0.339	0.459	0.9035	0.913 52	0.5357	0.090	0.121
0.3478	1.095 81	1.3034	0.368	0.469	0.9631	0.893 26	0.4850	0.032	0.052
0.4095	1.076 79	1.1712	0.406	0.478	1.0000	0.880 72	0.4630	0.000	0.000
$\nu_{12} = 0.7517$, $\nu_{21} = 1.1677$									
T = 308.15 K									
0.0000	1.189 70	2.0476	0.000	0.000	0.5621	1.019 55	0.8044	0.545	0.333
0.0524	1.174 80	1.8581	0.093	0.105	0.6094	1.004 12	0.7503	0.533	0.310
0.1036	1.159 60	1.7090	0.145	0.171	0.6479	0.991 30	0.7016	0.504	0.296
0.1429	1.148 34	1.5984	0.217	0.221	0.7082	0.971 23	0.6445	0.463	0.256
0.2064	1.129 41	1.4321	0.288	0.281	0.7635	0.952 53	0.5960	0.406	0.215
0.2431	1.118 55	1.3511	0.338	0.303	0.8388	0.926 67	0.5361	0.299	0.153
0.3083	1.098 84	1.2080	0.404	0.340	0.9035	0.904 41	0.4872	0.208	0.096
0.3478	1.086 81	1.1330	0.442	0.351	0.9631	0.880 35	0.4449	0.093	0.043
0.4095	1.067 88	1.0247	0.496	0.360	1.0000	0.870 33	0.4277	0.000	0.000
0.5098	1.036 38	0.8753	0.545	0.346					
$\nu_{12} = 0.6745$, $\nu_{21} = 1.0408$									
T = 318.15 K									
0.0000	1.177 96	1.7243	0.000	0.000	0.5621	1.011 79	0.7222	0.761	0.252
0.0524	1.164 57	1.5894	0.198	0.064	0.6094	0.996 65	0.6719	0.765	0.239
0.1036	1.149 88	1.4592	0.287	0.126	0.6479	0.984 06	0.6343	0.748	0.225
0.1429	1.138 89	1.3731	0.367	0.158	0.7082	0.964 25	0.5827	0.719	0.197
0.2064	1.120 24	1.2386	0.449	0.210	0.8062	0.931 69	0.5098	0.652	0.139
0.2431	1.109 88	1.1672	0.533	0.232	0.8388	0.920 53	0.4805	0.604	0.125
0.3083	1.090 41	1.0565	0.608	0.256	0.9035	0.899 34	0.4425	0.454	0.076
0.3478	1.078 57	0.9920	0.654	0.268	0.9631	0.875 70	0.4040	0.213	0.035
0.5098	1.028 37	0.7782	0.750	0.266	1.0000	0.861 40	0.3902	0.000	0.000
$\nu_{12} = 0.5981$, $\nu_{21} = 0.9404$									
Propylene Carbonate (1) + Methanol (2)									
T = 298.15 K									
0.0000	1.198 83	2.4711	0.000	0.000	0.5124	1.066 48	1.1069	0.324	0.377
0.0512	1.189 00	2.2662	0.038	0.106	0.5819	1.040 09	1.0009	0.341	0.349
0.0983	1.179 59	2.0971	0.081	0.184	0.6762	0.999 33	0.8678	0.357	0.300
0.1406	1.170 72	1.9579	0.121	0.242	0.7580	0.958 20	0.7707	0.353	0.239
0.1883	1.160 07	1.8106	0.159	0.298	0.8297	0.916 68	0.6887	0.331	0.183
0.2587	1.142 83	1.6157	0.191	0.357	0.9256	0.849 86	0.5981	0.203	0.089
0.3430	1.120 18	1.4144	0.232	0.396	0.9495	0.830 21	0.5805	0.120	0.060
0.3986	1.104 08	1.2982	0.273	0.405	1.0000	0.786 63	0.5437	0.000	0.000
0.4723	1.080 32	1.1670	0.300	0.394					
$\nu_{12} = 0.9084$, $\nu_{21} = 1.2641$									
T = 308.15 K									
0.0000	1.189 70	2.0476	0.000	0.000	0.5124	1.057 38	0.9480	0.362	0.296
0.0512	1.179 91	1.8952	0.045	0.072	0.5819	1.031 07	0.8651	0.387	0.270
0.0983	1.170 95	1.7572	0.123	0.136	0.6762	0.994 25	0.7581	0.412	0.229
0.1406	1.161 78	1.6479	0.146	0.179	0.8297	0.907 79	0.6034	0.383	0.143
0.1883	1.150 91	1.5334	0.173	0.219	0.8931	0.865 30	0.5517	0.312	0.096
0.2587	1.133 89	1.3773	0.224	0.265	0.9256	0.841 55	0.5282	0.277	0.068
0.3430	1.111 19	1.2129	0.267	0.297	0.9495	0.822 10	0.5118	0.201	0.047
0.4723	1.071 51	1.0020	0.354	0.305	1.000	0.777 18	0.4799	0.000	0.000
$\nu_{12} = 0.7847$, $\nu_{21} = 1.1093$									
T = 318.15 K									
0.0000	1.177 96	1.7234	0.000	0.000	0.4723	1.062 78	0.8683	0.530	0.240
0.0512	1.168 75	1.5939	0.088	0.063	0.5124	1.048 79	0.8232	0.541	0.233
0.0983	1.159 27	1.4804	0.129	0.115	0.5819	1.022 51	0.7459	0.559	0.211
0.1406	1.150 85	1.3931	0.203	0.147	0.8297	0.899 05	0.5281	0.503	0.115
0.1883	1.140 50	1.2958	0.264	0.182	0.8931	0.856 58	0.4829	0.416	0.078
0.2587	1.124 10	1.1688	0.353	0.218	0.9256	0.832 04	0.4621	0.332	0.056
0.3430	1.101 99	1.0340	0.427	0.243	0.9495	0.813 01	0.4486	0.270	0.039
0.3986	1.085 92	0.9607	0.468	0.244	1.0000	0.767 20	0.4216	0.000	0.000
$\nu_{12} = 0.6933$, $\nu_{21} = 0.9509$									

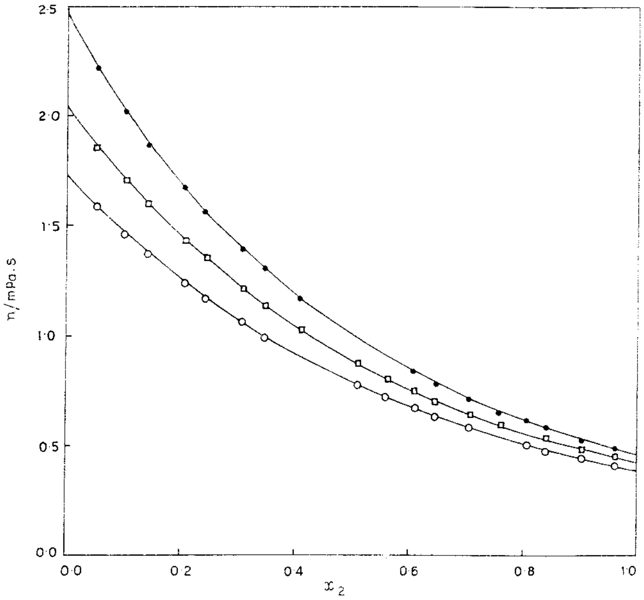

Figure 1. Viscosities (η) for the binary mixtures of propylene carbonate (1) + tetrahydrofuran (2) at 298.15 (●), 308.15 (□), and 318.15 (○).

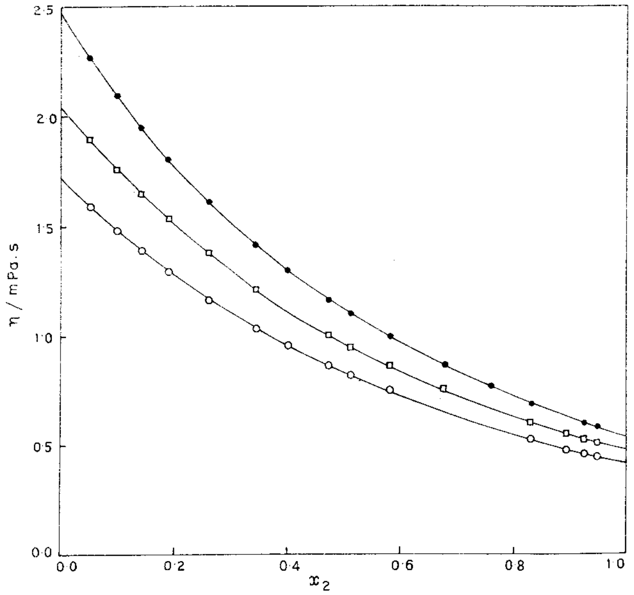

Figure 2. Viscosities (η) for the binary mixtures of propylene carbonate (1) + methanol (2) at 298.15 (●), 308.15 (□), and 318.15 (○).

(Muhuri and Hazra, 1994) by us:

$$\ln \nu = x_1^3 \ln \nu_1 M_1 + x_2^3 \ln \nu_2 M_2 - \ln(x_1 M_1 + x_2 M_2) + 3x_1^2 x_2 \ln \nu_{12}[(2M_1 + M_2)/3] + 3x_2^2 x_1 \ln \nu_{21}[(2M_2 + M_1)/3] \quad (3)$$

The interaction parameters, ν_{ij}, are also reported in Table 1.

The excess molar volumes have been calculated by the following equation:

$$V^E = V - (V_1 x_1 + V_2 x_2) \quad (4)$$

The deviation of the viscosity from the mole fraction average is calculated from

$$\Delta\eta = \eta - (\eta_1 x_1 + \eta_2 x_2) \quad (5)$$

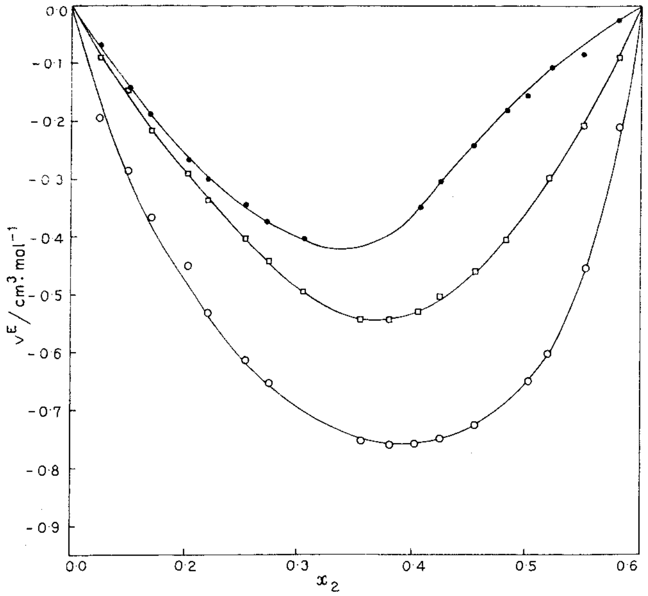

Figure 3. Excess molar volumes (V^E) for the binary mixtures of propylene carbonate (1) + tetrahydrofuran (2) at 298.15 (●), 308.15 (□), and 318.15 (○).

x_1 and x_2 are the mole fractions of components 1 and 2, respectively, V, V_1, and V_2 are the molar volumes, and η, η_1, and η_2 are the measured absolute viscosities of the mixture, component 1, and component 2, respectively. The molar volume V is defined by the relationship

$$V = (M_1 x_1 + M_2 x_2)/\rho \quad (6)$$

where M_1 and M_2 are the molecular weights of the pure substances and ρ is the density of the mixture.

The excess molar volumes at (298.15, 308.15, and 318.15) K are presented in Table 1.

The excess molar volumes (V^E) and the viscosity deviations ($\Delta\eta$), have been fitted to the Redlich–Kister relation (Redlich and Kister, 1948):

$$F = x_1(1 - x_1)\sum_{j=0}^{n} A_j (1 - 2x_1)^j \quad (7)$$

where $F = V^E$ or $\Delta\eta$ and A_0, A_1, A_2, ... are adjustable parameters and were evaluated by the method of least squares. The values of these parameters along with the standard deviation

$$\sigma(F) = [\sum(F_{\text{obsd}} - F_{\text{calcd}})^2/(N - P)]^{1/2} \quad (8)$$

are recorded in Table 2. In eq 8, N is the total number of experimental points and P is the number of parameters.

Figures 3 and 4 show the experimental points of V^E plotted against x_2 as well as the curves fitted by eq 7 with the parameters reported in Table 2.

Discussion

The kinematic viscosity data for the binary solvent mixtures were correlated with the McAllister equation of three-body interactions. In both systems the values of ν_{ij} are found to change with temperature. From Table 1, it is observed that for both systems and at each temperature the values of ν_{12} are less than the corresponding ν_{21} values. This indicates that the magnitudes of the interaction terms of propylene carbonate–propylene carbonate–tetrahydrofuran and propylene carbonate–propylene carbonate–

Table 2. Coefficients of Eq 7 and the Standard Deviations

function	T/K	A_0	A_1	A_2	A_3	A_4	$\sigma(F)$
		Propylene Carbonate (1) + Tetrahydrofuran (2)					
V^E/cm^3·mol^{-1}	298.15	−1.5753	−0.6710	1.0392	0.4804	−0.6790	0.012
	308.15	−2.1799	0.4211	1.0100	−0.0240	−1.2610	0.007
	318.15	−3.0046	0.9241	−0.4780	0.2448	−2.2059	0.017
$\Delta\eta$/mPa·s	298.15	−1.8582	−0.6661	−0.1397	−0.1191	−0.2310	0.004
	308.15	−1.4198	−0.4252	−0.1714	−0.0984	−0.5239	0.004
	318.15	−1.0778	−0.3930	−0.0057	0.2345	−0.0852	0.003
		Propylene Carbonate (1) + Methanol (2)					
V^E/cm^3·mol^{-1}	298.15	−1.2160	0.8540	−1.4431	0.2948	0.9537	0.012
	308.15	−1.4192	0.6055	−0.9593	1.3855	−0.7141	0.016
	318.15	−2.1560	0.6085	0.0096	1.8400	−2.2453	0.011
$\Delta\eta$/mPa·s	298.15	−1.5631	−0.6403	−0.1394	0.1970	−0.0677	0.011
	308.15	−1.1825	−0.4085	−0.1675	0.1499	0.1057	0.003
	318.15	−0.9375	−0.3505	−0.2078	0.1006	0.0737	0.002

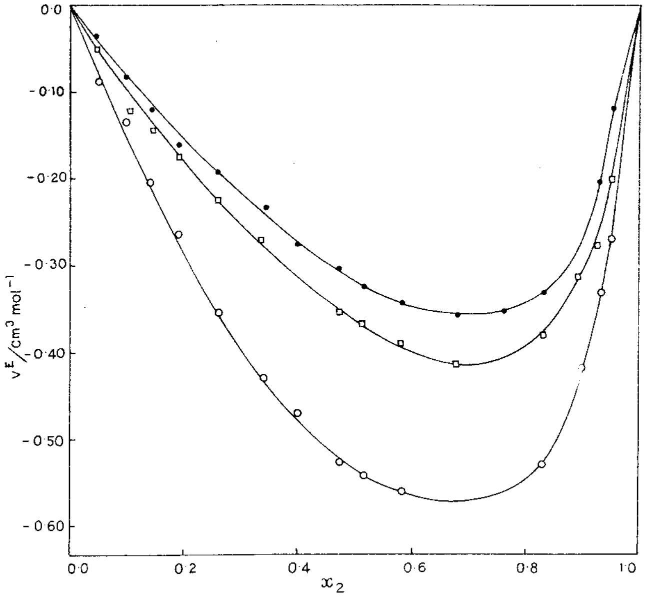

Figure 4. Excess molar volumes (V^E) for the binary mixtures of propylene carbonate (1) + methanol (2) at 298.15 (●), 308.15 (□), and 318.15 (○).

methanol are greater than those originating from the corresponding tetrahydrofuran−tetrahydrofuran−propylene carbonate and methanol−methanol−propylene carbonate interactions in propylene carbonate + tetrahydrofuran and propylene carbonate + methanol solvent mixtures, respectively. Further, the values of ν_{ij} and ν_{ji} decrease with temperature, in general, for both systems. Similar results have also been observed in other nonaqueous−nonaqueous solvent mixtures (Dizechi and Marschall, 1982).

Figures 1 and 2 show that the viscosities of both systems increase gradually with an increase in the propylene carbonate content in the mixture. The absence of any maxima in the intermediate composition gives an indication of the possible absence of specific interaction between propylene carbonate and methanol or between propylene carbonate and tetrahydrofuran.

In propylene carbonate + tetrahydrofuran solvent mixtures, the excess molar volumes at different temperatures are negative over the whole range of compositions (Figure 3). The magnitude of V^E increases with an increase in temperature. The minima of V^E appear at a mole fraction of 0.5. It appears that on mixing tetrahydrofuran with propylene carbonate, the dipole−dipole interactions between propylene carbonate become weaker and the dipolar interactions between unlike molecules predominate, as a result of which a sharp decrease in volume occurs.

In the propylene carbonate + methanol binary system, the excess molar volumes are negative at each temperature, the values of V^E decrease further, and the minima of V^E appear in the vicinity of 0.7 mole fraction of methanol, as shown in Figure 4. The molar volumes of propylene carbonate and methanol at 25 °C are 85.16 and 40.73 cm^3·mol^{-1}, respectively, which might allow the components to fit into each other's structure, causing the reduction in volume of the mixture.

Literature Cited

Covington, A. K.; Dickinson, T. *Physical Chemistry of Organic Solvent Systems*; Plenum Press: New York, 1973.

Dizechi, M.; Marshall, E. Viscosity of Some Binary and Ternary Liquid Mixtures. *J. Chem. Eng. Data* **1982**, *27*, 358−363.

Grast, J. F. *Solute-Solvent Interactions*; Marcel Dekker: New York, 1969.

Jansen, M. L.; Yeager, H. L. Conductance Study of 1-1 Electrolytes in propylene Carbonate. *J. Phys. Chem.* **1973**, *77*, 3089−3092.

Jansen, M. L.; Yeager, H. L. Conductance Measurements of Alkali Metal Trifluoroacetates in Propylene Carbonate. *J. Phys. Chem.* **1974**, *78*, 1380−1382.

Jasinski, R. J. *High Energy Batteries*; Plenum Press: New York, 1967a.

Jasinski, R. J. Bibliography on the Uses of Propylene Carbonate in High Energy Batteries. *J. Electroanal. Chem.* **1967b**, *15*, 89−91.

Matsuda, Y.; Satake, H. Mixed Electrolyte Solutions of Propylene Carbonate and Dimethoxyethane for High Energy Batteries. *J. Electroanal. Chem.* **1980**, *127*, 877−879.

Moumouzias, G.; Panopoulos, D. K.; Ritzoulis, G. Excess Properties of the Binary Liquid System Propylene Carbonate + Acetonitrile. *J. Chem. Eng. Data* **1991**, *36*, 20−25.

Muhuri, P. K.; Hazra, D. K. Density and Viscosity for Propylene Carbonate + 1,2-Dimethoxyethane at 298.15, 308.15 and 318.15 K. *J. Chem. Eng. Data* **1994**, *39*, 375−377.

Muhuri, P. K.; Hazra, D. K. Density and Viscosity of Propylene Carbonate + 2-Methoxyethanol at 298.15, 308.15 and 318.15 K. *J. Chem. Eng. Data* **1995**, *40*, 582−585.

Redlich, O.; Kister, A. T. Thermodynamics of Nonelectrolytic Solutions. Algebraic Representation of Thermodynamic Properties of the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

Ritzoulis, G. Excess Properties of the Binary Liquid Systems Dimethylsulfoxide + Isopropanol and Propylene Carbonate and Propylene Carbonate + Isopropanol. *Can. J. Chem.* **1989**, *67*, 1105−1108.

Saha, N.; Das, B.; Hazra, D. K. Viscosities and Excess Molar Volumes for Acetonitrile + Methanol at 298.15, 308.15, and 318.15 K. *J. Chem. Eng. Data* **1995**, *40*, 1264−1266.

Received for review June 6, 1996. Accepted August 13, 1996.[⊗] P.K.M. thanks CSIR, India, for providing a research associateship. Financial assistance from CSIR Extramural research is gratefully acknowledged.

JE960196B

[⊗] Abstract published in *Advance ACS Abstracts*, September 15, 1996.