Density, Viscosity, and Excess Properties of Binary Liquid Mixtures of Propylene Carbonate with Polar and Nonpolar Solvents

Pragati Jain and Mukhtar Singh*

Department of Chemistry, Agra College, Agra-282002, India

The density and viscosity of binary liquid mixtures of propylene carbonate with polar and nonpolar solvents (acetone, chloroform, 1,4-dioxane benzene, toluene, and *o*-xylene) have been measured at 303.15 K. From density and viscosity data, the values of excess molar volume (V^E) and deviations in viscosity ($\delta\eta$) have been determined. The excess molar volume and deviations in viscosity are negative over the entire range of composition. The density and viscosity data have been theoretically analyzed for the validity of different viscosity models.

Introduction

Propylene carbonate is identified as an outstanding dipolar aprotic solvent, widely used in extractions and in electrochemical studies. Some lithium batteries have adopted mixed organic electrolytes containing propylene carbonate because their molecules have no active hydrogen atoms reacting with lithium, which prevents the evolution of hydrogen into the cell. Furthermore, it was found that mixtures of more electrolytes present improved electrical properties compared with those of a pure solvent so that the studies of the physical properties of mixtures containing propylene carbonate are important. This prompted Comelli and Francesconi[1] to undertake studies relating to the determination of excess molar enthalpies and excess molar volumes of binary mixtures of propylene carbonate with cyclic ethers (oxane, oxolane, 1,4-dioxane, and 1,3-dioxolane) and linear and cyclic ketones[2] (eight methyl *n*-alkyl ketones + three cyclic ketones) at 298.15 K. The results have been correlated using the Redlich−Kister[3] equation, and the parameters have been evaluated by least-squares analysis.

Konti and co-workers[4] have reported studies on the determination of densities, relative permittivities, and refractive indices of propylene carbonate with *p*-xylene at (15, 20, 25, 30, and 35) °C. The excess molar volumes and deviations in relative permittivities and molar refraction have been found to be negative. The negative values of V^E have been attributed to the different size of propylene carbonate and *p*-xylene molecules and to the specific interactions due to a dipole−induced dipole effect.

Recently, Zhao and co-workers[5] studied the effect of temperature on excess molar volumes and viscosities for propylene carbonate + *N*,*N*-dimethylformamide mixtures. Densities and viscosities have been determined as a function of mole fraction for propylene carbonate + *N*,*N*-dimethylformamide mixtures at (298.15, 308.15, 318.15, and 338.15) K. From these measurements, the excess molar volume (V^E) and deviations in viscosity ($\delta\eta$) were calculated. The results were fit to the Redlich−Kister polynomials. The values of V^E are found to be positive, whereas the $\delta\eta$ are negative over the entire range of composition at each temperature investigated. The values of V^E decrease, but those of $\delta\eta$ increase with increasing temperature. Results have been explained on the basis of molecular interactions in the mixtures.

There are relatively few studies on the excess volume (V^E) and viscosity deviations ($\delta\eta$) for the binary mixtures of propylene carbonate with polar and nonpolar solvents, so we present in this paper new experimental data on densities and viscosities for the binary mixtures of propylene carbonate with polar and nonpolar (acetone, 1,4-dioxane, chloroform, benzene, toluene, and *o*-xylene) solvents at 303.15 K.

Experimental Section

Chemicals. All chemicals were from Aldrich, and their purities were better than 99 mol %. The purities of the compounds were checked by density determinations at (303.15 ± 0.01) K by using a vibrating digital density meter (Anton Parr, model 60/602, Austria), and the values obtained are reported in Table 1 and compared with literature values. Before measurements, the liquids were dried over molecular sieves (Union Carbide, type 4A, $^1/_{16}$ in. pellets) and kept in dark bottles.

Measurements. Liquid mixtures of various compositions were prepared by weight in a 25-cm^3 flask using a Mettler analytical balance. The corresponding accuracy in the mole fraction calculation was better than ±0.0001. Density and viscosity measurements were carried out using a thermostatically controlled, well-stirred water bath, where temperatures were measured with a digital thermometer with an accuracy of ±0.01 K. A proportional integral control model was used to maintain the temperature in the thermostat to be within ±0.01K of the desired value.

Densities of pure liquids and binary liquid mixtures were measured at 303.15 K with an Anton Parr digital vibrating tube densimeter (model 60/602, Anton Parr, Austria). The densimeter was calibrated with degassed water and dehumidified air at atmospheric pressure. More than eight readings were taken for each density measurement. The accuracy of the density values was better than $\pm 5 \times 10^{-5}$ gm cm^{-3}, and that of excess volume values was ±0.007 cm^3 mol^{-1}.

The viscosities (η) of pure organic liquids and their binary mixtures were determined with an accuracy of ±3

---

* Address for correspondence. H.I.G., 142 Shastri Puram, P. O. Sikandra, Agra-282007, India. E-mail: mukhtarsingh2003@rediffmail.com.

10.1021/je034204h CCC: $27.50

Table 1. Comparison of Experimental Density and Viscosity of Pure Liquids with Literature Values at 303.15 K

pure liquid	ρ (gm·cm^{-3}) exptl	ρ (gm·cm^{-3}) lit	η(mPa·s) exptl	η(mPa·s) lit
propylene carbonate	1.1945	1.1926[a]	2.1494	2.508[b,i]
acetone	0.7824	0.7848[c,i]	0.2975	0.2950[d]
1,4-dioxane	1.0233	1.0223[e]	1.0224	1.0505[d]
chloroform	1.4609	1.4628[d]	0.5033	0.5249[d]
benzene	0.8659	0.8684[f]	0.5390	0.603[g,i]
toluene	0.8604	0.8576[h]	0.5229	0.552[g,i]
o-xylene	0.8605	0.8758[g,i]	0.7272	0.754[g,i]

[a] Konti et al.[4] [b] Zhao et al.[5] [c] Comelli and Francesconi.[2] [d] Lide.[15] [e] Krishnaiah et al.[16] [f] Viswanathan et al.[17] [g] Gupta and Singh.[18] [h] Ramadevi and Rao.[19] [i] At 298.15 K.

× 10^{-3} mPa·s using an Ostwald viscometer, which was suspended in a thermostat maintained at 303.15 ± 0.01 K. The details of the procedure have been reported in an earlier publication.[6]

Results and Discussion

The excess molar volume (V^E) of the binary liquid mixture has been determined from the molar volume (V) of the mixtures and that of the pure components (V_1 and V_2) using the following relation[7]

$$V^E = V - (x_1V_1 + x_2V_2) \tag{1}$$

The molar volume of the mixtures (V) has been computed from the measured density using the equation

$$V = \frac{x_1M_1 + x_2M_2}{\rho} \tag{2}$$

where x_1 and x_2 are the mole fractions of components 1 and 2 of the binary mixtures, respectively. V_1 is M_1/ρ_1, and V_2 is M_2/ρ_2.

The deviation in viscosity ($\delta\eta$) of the binary liquid mixture has been evaluated from the observed viscosity of the mixture (η) and that of the individual components (η_1 and η_2) using the equation[7]

$$\delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \tag{3}$$

where x_1 and x_2 are the mole fractions of components 1 and 2, respectively.

Deviation in Viscosity ($\delta\eta$). It is seen that the values of $\delta\eta$ (vide Table 2) for binary mixtures of propylene carbonate with polar and nonpolar solvents are negative over the entire range of composition. The negative values of $\delta\eta$ may be attributed to the dominance of dispersion forces between the mixing components of the binary mixtures under discussion.[8]

The plots of $\delta\eta$ versus x_1 have been presented in Figure 1. It is seen that the plots are parabolic and are characterized by the presence of well-defined minima occurring at $x_1 \approx 0.5$. These minima indicate the presence of complex formation with 1:1 composition.

Excess Molar Volume (V^E). The values of V^E have been presented in Table 2. It is seen that the values of V^E for the binary mixtures of propylene carbonate with polar solvents (acetone and chloroform) and nonpolar solvents (benzene, toluene, *o*-xylene, and 1,4-dioxane) are negative over the entire range of composition, suggesting specific interactions[9] between the mixing components. The chemical or specific interactions between constituent molecules of the mixture result in a volume decrease.

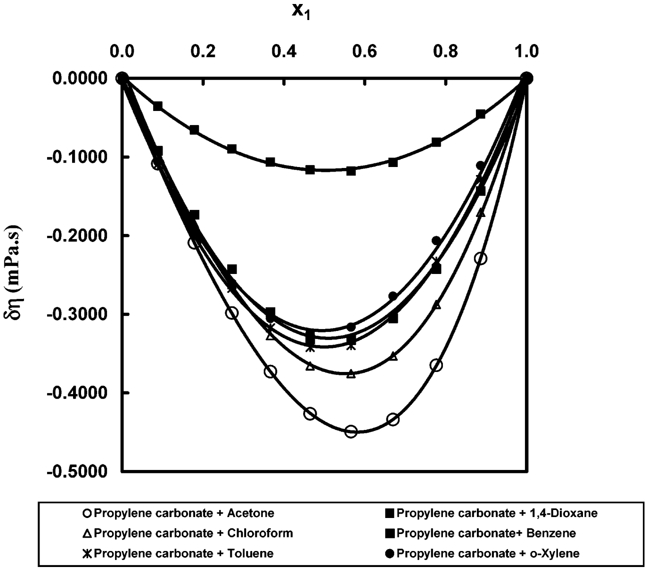

Figure 1. Variation of viscosity deviations ($\delta\eta$) with mole fraction (x_1) of propylene carbonate in binary liquid mixture of propylene carbonate with acetone, 1,4-dioxane, chloroform, benzene, toluene, and *o*-xylene at 303.15 K.

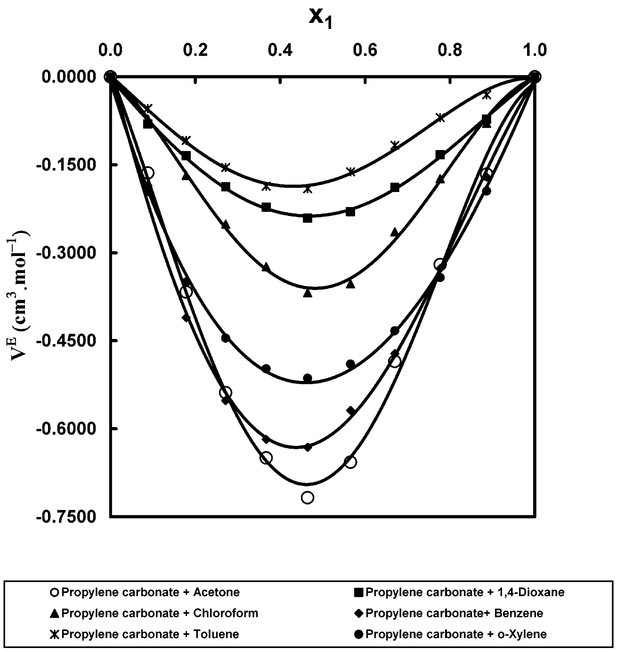

Figure 2. Variation of excess molar volume (V^E) with mole fraction (x_1) of propylene carbonate in binary liquid mixtures of propylene carbonate with acetone, 1,4-dioxane, chloroform, benzene, toluene, and *o*-xylene at 303.15 K.

The negative values of V^E in the case of binary mixtures of propylene carbonate with acetone may be attributed to the dipole−dipole interactions resulting in the formation of electron-transfer complexes between the molecules of mixing components. The negative values of V^E for the binary mixtures of propylene carbonate with nonpolar solvents (benzene, toluene, 1,4-dioxane, and *o*-xylene) may be attributed to the dipole−induced dipole interactions between the mixing components resulting in the formation of electron donor−acceptor complexes.

The plots of V^E versus x_1 have been presented in Figure 2. A perusal of these Figures shows that in each case the plots are parabolic and are characterized by the presence of well-defined minima that occur at $x_1 \approx 0.5$, indicating

Table 2. Densities (ρ), Viscosities (η), Excess Molar Volumes (V^E), and Deviations in Viscosity ($\delta\eta$) for Binary Liquid Mixtures of Propylene Carbonate with Polar and Nonpolar Solvents at 303.15 K

x_1	ρ g·cm^{-3}	η mPa·s	$\delta\eta$ mPa·s	V^E cm^3·mol^{-1}	x_1	ρ g·cm^{-3}	η mPa·s	$\delta\eta$ mPa·s	V^E cm^3·mol^{-1}
Propylene Carbonate + Acetone System									
0	0.7824	0.2974	0	0	0.5657	1.0381	0.8959	−0.4492	−0.6569
0.088	0.8254	0.3518	−0.1086	−0.1637	0.6697	1.0773	1.104	−0.4337	−0.4851
0.1784	0.869	0.4187	−0.2091	−0.3668	0.7768	1.1165	1.3713	−0.3647	−0.3199
0.2713	0.9124	0.5016	−0.2982	−0.5382	0.8864	1.1555	1.71	−0.229	−0.166
0.3668	0.9552	0.6038	−0.3729	−0.6496	1	1.1945	2.1494	0	0
0.4647	0.9974	0.7316	−0.4264	−0.7172					
Propylene Carbonate + 1,4-Dioxane System									
0	1.0233	1.0224	0	0	0.6015	1.129	1.5824	−0.1179	−0.23
0.1007	1.0414	1.1004	−0.0355	−0.081	0.7018	1.1457	1.7063	−0.107	−0.188
0.2012	1.0592	1.1837	−0.0655	−0.135	0.8014	1.1621	1.8444	−0.0812	−0.133
0.3015	1.077	1.2726	−0.0896	−0.188	0.9008	1.1784	1.992	−0.0456	−0.072
0.4017	1.0946	1.3686	−0.1065	−0.222	1	1.1945	2.1494	0	0
0.5017	1.112	1.4715	−0.1163	−0.241					
Propylene Carbonate + Chloroform System									
0	1.4609	0.5033	0	0	0.5894	1.3065	1.0981	−0.3754	−0.3531
0.0961	1.4355	0.5649	−0.0966	−0.0719	0.6906	1.2784	1.287	−0.3531	−0.2643
0.1929	1.4105	0.6358	−0.185	−0.168	0.7925	1.2504	1.5203	−0.2875	−0.1735
0.2906	1.3852	0.7195	−0.2622	−0.2513	0.8962	1.2222	1.808	−0.1705	−0.0794
0.3894	1.3596	0.8171	−0.3272	−0.3238	1	1.1945	2.1494	0	0
0.4887	1.3336	0.9421	−0.3656	−0.3683					
Propylene Carbonate + Benzene System									
0	0.8659	0.539	0	0	0.6131	1.0701	1.1937	−0.3326	−0.568
0.1049	0.9006	0.616	−0.0919	−0.185	0.7109	1.1018	1.3788	−0.305	−0.472
0.2087	0.9359	0.7019	−0.1732	−0.410	0.8083	1.133	1.5986	−0.2421	−0.327
0.3114	0.9705	0.798	−0.2425	−0.552	0.9046	1.1639	1.8528	−0.143	−0.171
0.4131	1.0044	0.9074	−0.2969	−0.618	1	1.1945	2.1494	0	0
0.5136	1.0377	1.0345	−0.3316	−0.631					
Propylene Carbonate + Toluene System									
0	0.8604	0.5229	0	0	0.6524	1.0626	1.2444	−0.3396	−0.1621
0.1223	0.8943	0.6125	−0.1093	−0.0542	0.7452	1.0957	1.4313	−0.3037	−0.1168
0.2385	0.9282	0.7127	−0.1981	−0.1086	0.8335	1.1285	1.6461	−0.2325	−0.0698
0.3493	0.9621	0.824	−0.267	−0.1547	0.9188	1.1616	1.8885	−0.1288	−0.0306
0.4553	0.996	0.9463	−0.3171	−0.1863	1	1.1945	2.1494	0	0
0.5561	1.0295	1.0853	−0.3421	−0.1908					
Propylene Carbonate + *o*-Xylene System									
0	0.8605	0.7272	0	0	0.6842	1.0663	1.3841	−0.3162	−0.4897
0.1383	0.8954	0.8178	−0.1061	−0.1956	0.7712	1.0994	1.5471	−0.2769	−0.4329
0.2653	0.9302	0.9124	−0.1921	−0.3498	0.8525	1.132	1.7333	−0.2063	−0.3421
0.3824	0.9647	1.0108	−0.2602	−0.4453	0.9286	1.1637	1.937	−0.1109	−0.1948
0.4906	0.9989	1.1198	−0.3051	−0.4975	1	1.1945	2.1494	0	0
0.5909	1.0328	1.2435	−0.3241	−0.5139					

the presence of complex formation between the mixing components having a 1:1 composition ratio.

Viscosity Models and Interaction Parameters. With a view toward correlating the viscosities of binary liquid mixtures with those of component liquids and interpreting the molecular interactions in these mixtures, several equations have been put forward from time to time. These are given in the following text.

Grunberg and Nissan[10] have suggested the following logarithmic relation between the viscosity of the binary mixture and the pure components:

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d_{12} \tag{4}$$

where d_{12} is a constant proportional to the interchange energy (w). It may be regarded as an approximate measure of the strength of molecular interactions between the mixing components. The values of interaction parameter d_{12} have been calculated as a function of the composition of the binary liquid mixtures of propylene carbonate with polar and nonpolar solvents, and it has been found that the values of d_{12} are negative for all of the binary mixtures of propylene carbonate with polar and nonpolar solvents over the entire composition range. The negative values of d_{12} indicate the presence of dispersion forces[8]

Tamura−Kurata[11] put forward the following equation for the viscosity of binary liquid mixtures:

$$\eta = x_1\phi_1\eta_1 + x_2\phi_2\eta_2 + 2(x_1x_2\phi_1\phi_2)^{0.5}T_{12} \tag{5}$$

where T_{12} is the interaction parameter and ϕ_1 and ϕ_2 are the volume fractions of pure components 1 and 2, respectively.

Molecular interactions may also be interpreted by the following viscosity model of Hind et al.:[12]

$$\eta = x_1^2\eta_1 + x_2^2\eta_2 + 2x_1x_2H_{12} \tag{6}$$

where H_{12} is Hind interaction parameter.

In the present study, the values of interaction parameters T_{12} and H_{12} have been calculated from the corresponding equations (eqs 5 and 6, respectively), and it has been observed that for a given binary mixture T_{12} and H_{12} do not differ appreciably from each other. This is in agreement with the view put forward by Fort and Moore[8] in regard to the nature of parameters T_{12} and H_{12}.

Table 3. Values of McAllister Parameters (Z_{12} and Z_{21}) and Heric and Brewer Parameters (a, b, c) at 303.15 K

system	Z_{12}	Z_{21}	$a \times 10^2$ $\text{cm}^2\ \text{s}^{-1}$	$b \times 10^2$ $\text{cm}^2\ \text{s}^{-1}$	$c \times 10^2$ $\text{cm}^2\ \text{s}^{-1}$
propylene carbonate +					
acetone	1.1075	0.1911	−1.2530	−0.3701	−0.0432
chloroform	1.2111	0.2448	−1.4073	−0.4930	−0.0424
1,4-dioxane	1.6562	0.4346	−0.3116	−0.0653	0.0276
benzene	1.2578	0.2726	−0.9021	−0.2863	0.0568
toluene	1.2345	0.2667	−0.8408	−0.2991	0.0083
o-xylene	1.2760	0.3174	−0.7813	−0.3619	0.0192

McAllister,[13] on the basis of Eyring's three-body interaction model, has proposed the following equation for the viscosity (η) of binary liquid mixtures:

$$\ln \eta = x_1^3 \ln \eta_1 + 3x_1^2 x_2 \ln Z_{12} + 3x_1 x_2^2 \ln Z_{21} + x_2^3 \ln \eta_2 + \ln(x_1 + x_2(M_2/M_1)) + 3x_1^2 x_2 \ln\left[\frac{2 + (M_2/M_1)}{3}\right] + 3x_1 x_2^2 \ln\left[\frac{1 + 2(M_2/M_1)}{3}\right] + x_2^3 \ln(M_2/M_1) \tag{7}$$

where Z_{12} and Z_{21} are McAllister interaction parameters.

The values of Z_{12} and Z_{21} have been calculated and listed in Table 3. It is seen that the values of both the parameters are positive for all of the binary mixtures. Furthermore, the values of Z_{12} and Z_{21} are larger for the mixtures involving nonpolar solvents.

Heric and Brewer[14] have proposed an equation for the kinematic viscosity λ $(= {}^{\eta}/_{\rho})$ of the binary liquid mixtures:

$$\lambda = x_1\lambda_1 + x_2\lambda_2 + x_1x_2[a + b(x_1 - x_2) + \text{c}(x_1 - x_2)^2] \tag{8}$$

where λ_1 and λ_2 are the kinematic viscosities of components 1 and 2, respectively. The values of parameters a, b, and c have been calculated and listed in Table 3. A perusal of this Table shows that the values of a and b are negative for all of the binary mixtures of propylene carbonate with polar and nonpolar solvents; the values of c are negative for the binary mixtures involving polar solvents but positive for the ones involving nonpolar solvents.

Literature Cited

(1) Francesconi, R.; Comelli, F. Excess Molar Enthalpies and Excess Molar Volumes of Propylene Carbonate + Cyclic Ethers. *J. Chem. Eng. Data* **1995**, *40*, 31−33.

(2) Comelli, F.; Francesconi, R. Densities and Excess Molar Volumes of Propylene Carbonate + Linear and Cyclic Ketones at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 808−810.

(3) Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solution. *IInd Indian Eng. Chem*. **1948**, *40*, 345−.

(4) Konti, A.; Moumouzias, G.; Ritzoulis, G. Densities, Relative Permittivities, and Refractive Indices for the Binary Liquid System Propylene Carbonate + *p*-Xylene at (15, 20, 25, 30 and 35) °C. *J. Chem. Eng. Data* **1997**, *42*, 614−618.

(5) Zhao, Y.; Wang, J.; Xuan, X.; Lu, J. Effect of Temperature on Excess Molar Volumes and Viscosities for Propylene Carbonate + *N*, *N*-Dimethylformamide Mixtures. *J. Chem. Eng. Data* **2000**, *45*, 440−444.

(6) Singh, M.; Gupta, P. C.; Kesharwani, R. N. Density and Viscosity for Mixtures of Propanoic Acid with Aromatic Hydrocarbons at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 358−360.

(7) Weng, W. L. Densities and Viscosities for Binary Mixtures of Butylamine with Aliphatic Alcohols. *J. Chem. Eng. Data* **2000**, *45*, 606−609.

(8) Fort, R. J.; Moore, W. R. Viscosities of Binary Liquid Mixtures. *Trans. Faraday Soc.* **1966**, *62*, 1112−.

(9) Aminabhavi, T. M.; Kaikar, S. K.; Balundgi, R. H. Densities, Viscosities, Refractive Indices, and Speed of Sound in Methyl Acetoacetate + MethylAcetate, + *n*-Butyl Acetate, + Methyl Benzoate, and + Ethyl Benzoate at 298.15, 303.15, and 308.15 K. *J. Chem. Eng. Data* **1993**, *38*, 44-.

(10) Grunberg, L.; Nissan, A. H. Mixture Law for Viscosity. *Nature* **1949**, *164*, 799−.

(11) Tamura, M.; Kurata, M. Viscosity of Binary Mixture of Liquids. *Bull. Chem. Soc. Jpn*. **1952**, *25*, 32-.

(12) Hind, R. K.; McLaughlin, E.; Ubbelohde, A. R. Structure and Viscosity of Liquid-Camphor and Pyrene Mixtures. *Trans. Faraday Soc.* **1960**, *56*, 328-.

(13) McAllister, R. A. The Viscosity of Liquid Mixtures. *AIChE J*. **1960**, *6*, 427.

(14) Heric, E. L.; Brewer, J. G. Viscosity of Some Binary Liquid Nonelectrolyte Mixtures. *J. Chem. Eng. Data* **1967**, *12*, 574−583.

(15) Lide, D. R., Ed.; *CRC Handbook of Chemistry and Physics*, 75th ed. CRC Press: Boca Raton, FL, 1994.

(16) Krishnaiah, A.; Surendranath, K. N.; Viswanath, D. S. Excess Volumes and Viscosities of 1,4-Dioxane + Chlorinated Ethanes or + Chlorinated Ethenes at 303.15 K. *J. Chem. Eng. Data* **1994**, *39*, 756−758.

(17) Viswanathan, S.; Rao, M. A.; Prasad, D. H. L.; Rao, M. V. Excess Enthalpies for Anisol + Benzene, + Chlorobenzene, + Benzonitrile, and + Nitrobenzene at 298.15 K. *J. Chem. Eng. Data* **1996**, *41*, 173−174.

(18) Gupta, P. C.; Singh, M. Density and Viscosity of Binary Mixtures of *N*,*N*-Dimethylformamide with Aromatic Hydrocarbons at 298.15 K, vis-à-vis Molecular Interactions. *Indian J. Chem., Sect. A* **2001**, *40*, 293−297.

(19) Ramadevi, R. S.; Rao, M. V. P. Excess Volumes of Substituted Benzenes with *N*,*N*-Dimethylformamide. *J. Chem. Eng. Data* **1995**, *40*, 65−67.

Received for review October 17, 2003. Accepted June 2, 2004.

JE034204H