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Density and Viscosity for Propylene Carbonate + 1,2-Dimethoxyethane at 298.15, 308.15, and 318.15 K

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Densities and viscosities have been determined as a function of mole fraction for propylene carbonate + 1,2-dimethoxyethane at 298.15, 308.15, and 318.15 K. The excess molar volumes (V_m^E) have been calculated from the results. The values of V_m^E are found to be negative over the entire composition range and at all three temperatures studied. Kinematic viscosity data have been used to calculate the interaction parameters (ν_{12} and ν_{21}) for the three-body interactions of the McAllister equation.

Introduction

Both 1,2-dimethoxyethane (DME) and propylene carbonate (PC) find a wide range of applications as solvents and solubilizing agents in organic synthesis and electrochemical studies (*1–6*), but there are relatively very few thermodynamic studies of their aqueous and nonaqueous solution mixtures (*7–9*). In the present study, the density and viscosity have been measured for PC + DME mixtures over the entire composition range at three different temperatures. The interaction parameters (ν_{ij}) of the McAllister equation (*10*) for these systems have been determined from the kinematic viscosity results.

Experimental Section

Propylene carbonate (E. Merck, Germany; >99% pure) was dried over freshly ignited quicklime for several hours and then distilled three times under reduced pressure under nitrogen, the middle fraction being taken each time (*11*). The purified sample had a density of 1.1988 g·cm^{-3} and viscosity of 2.4711 mPa·s at 298.15 K. These values are in good agreement with the literature values which are 1.1993 g·cm^{-3} (*12*) and 2.480 mPa·s (*13*), respectively.

1,2-Dimethoxyethane (Fluka, purum) was shaken well with $FeSO_4$ (A.R., BDH) for 1–2 h, decanted, and distilled. The distillate was refluxed for 12 h and distilled over metallic sodium (*14*). The boiling point (357.5 K) and density (0.8613 g·cm^{-3} at 298.15 K) compared fairly well with the literature values (*15*): 358.15 K and 0.8612 g·cm^{-3}, respectively.

The densities 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 1 mm. The pycnometer was calibrated at 298.15, 308.15, and 318.15 K with doubly distilled water. The temperature control was accurate to ±0.01 K. The kinematic viscosities were measured at the desired temperature (accurate to ±0.01 K) using a suspended Ubbelohde-type viscometer (*16*). The precisions of density and viscosity measurements were $\pm 3 \times 10^{-5}$ g·cm^{-3} and ±0.05%, respectively. The kinematic viscosities were converted into absolute viscosities by multiplying the former by the density.

In all the cases, the experiments were performed in triplicate at each mole fraction and at each temperature and the results were averaged.

Results

The experimental results of density and viscosity measurements at various mole fractions are reported in Table 1.

The plots of viscosity (η) against the mole fraction of DME are given in Figure 1.

The kinematic viscosity data have been analyzed by means of the McAllister equation (*10*):

$$\ln \nu = x^3 \ln \nu_1 M_1 + (1-x)^3 \ln \nu_2 M_2 - \ln[xM_1 + (1-x)M_2] + 3x^2(1-x) \ln \nu_{12}\left(\frac{2M_1 + M_2}{3}\right) + 3(1-x)^2 x \ln \nu_{21}\left(\frac{2M_2 + M_1}{3}\right) \quad (1)$$

The interaction parameters, ν_{ij}, along with the kinematic viscosity data at different temperatures have also been reported in Table 1.

The excess molar volume was calculated by the following equation:

$$V_m^E = [xM_1 + (1-x)M_2]/\rho - xM_1/\rho_1 - (1-x)M_2/\rho_2 \quad (2)$$

where x is the mole fraction of DME, ρ, ρ_1, and ρ_2 are the corresponding densities of the mixture, DME, and PC, and M_1 and M_2 are the molecular weights of DME and PC, respectively.

The excess molar volumes have been presented in Table 2.

The plots of V_m^E against the mole fraction of DME are given in Figure 2.

The excess volume was fitted to the Redlich–Kister equation (*17*):

$$V_m^E/(\text{cm}^3\cdot\text{mol}^{-1}) = x(1-x)\sum_{j=0}^{n} A_j(2x-1)^j \quad (3)$$

where A_0, A_1, A_2, etc. are adjustable parameters and were evaluated by the method of least squares. The values of these parameters along with the standard deviations (σ^E) of V_m^E as defined by

$$\sigma^E = \left[\frac{\sum \omega(V_{m\,\text{exptl}}^{E} - V_{m\,\text{calcd}}^{E})^2}{(N-M)}\right]^{0.5} \quad (4)$$

are recorded in Table 3. In eq 4, N is the total number of experimental points and M is the number of adjustable parameters.

Discussion

In the interaction parameters ν_{ij}, the subscript ij refers to the interaction of the type *i–i–j*. The values of ν_{ij} change

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Table 1. Density (ρ), Absolute Viscosity (η), and Interaction Parameter (ν_{ij}) Results for (1 − x) Propylene Carbonate + x 1,2-Dimethoxyethane at 298.15, 308.15, and 318.15 K

x	ρ/(g·cm^{-3})	η/(mPa·s)	ν_{12}	ν_{21}	x	ρ/(g·cm^{-3})	η/(mPa·s)	ν_{12}	ν_{21}
				298.15 K					
0.0000	1.198 83	2.4711			0.5193	1.016 09	0.8882		
0.0493	1.180 24	2.2270			0.6382	0.976 83	0.7272		
0.0999	1.162 06	1.9600			0.6767	0.963 94	0.6885		
0.1524	1.142 35	1.7518			0.7589	0.937 05	0.6047		
0.1867	1.130 33	1.6366			0.8103	0.920 58	0.5589		
0.2298	1.114 68	1.5075			0.8432	0.910 34	0.5429		
0.3128	1.086 43	1.2889			0.9035	0.891 35	0.4872		
0.3708	1.065 94	1.1617			0.9483	0.876 95	0.4564		
0.4036	1.055 26	1.0974	0.7566	0.9687	1.0000	0.861 32	0.4236		
0.4686	1.040 97	0.9699							
				308.15 K					
0.0000	1.189 70	2.0476			0.5193	1.006 22	0.7779		
0.0493	1.171 17	1.8332			0.5704	0.989 53	0.7178	0.6214	0.9547
0.0999	1.152 34	1.6589			0.6767	0.956 13	0.6105		
0.1524	1.133 49	1.4955			0.8103	0.914 68	0.5052		
0.1867	1.120 93	1.4019			0.8432	0.904 50	0.4728		
0.2298	1.105 59	1.2966			0.9035	0.885 18	0.4381		
0.2769	1.088 43	1.1828			0.9483	0.870 25	0.4073		
0.3708	1.055 60	0.9973			1.0000	0.851 29	0.3847		
0.4036	1.044 82	0.9447							
				318.15 K					
0.0000	1.177 96	1.7234			0.5704	0.981 37	0.6389		
0.0493	1.159 99	1.5614			0.6382	0.958 58	0.5728		
0.0999	1.141 85	1.4166			0.6767	0.945 47	0.5449		
0.1524	1.123 02	1.2766			0.7589	0.918 10	0.4782		
0.2298	1.096 38	1.1130			0.8103	0.901 16	0.4571		
0.3128	1.068 19	0.9676			0.8432	0.890 78	0.4376		
0.3708	1.048 42	0.8810			0.9035	0.871 44	0.3970		
0.4036	1.037 67	0.8272			0.9483	0.856 67	0.3750		
0.5193	0.998 56	0.6827	0.5700	0.8230	1.0000	0.840 76	0.3496		

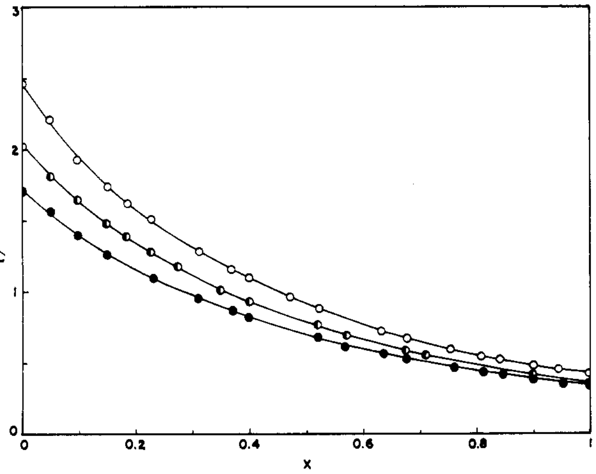

Figure 1. Viscosities for the binary mixtures of x DME + (1 − x) PC: ○, 298.15 K; ◐, 308.15 K; ●, 318.15 K.

Table 2. Excess Molar Volumes V_m^E for x 1,2-Dimethoxyethane + (1 − x) Propylene Carbonate

x	V_m^E/(cm^3·mol^{-1})	x	V_m^E/(cm^3·mol^{-1})	x	V_m^E/(cm^3·mol^{-1})
			298.15 K		
0.0000	0.0000	0.3708	−0.7678	0.7589	−0.6817
0.0493	−0.1186	0.4036	−0.8514	0.8103	−0.5743
0.0999	−0.2794	0.4686	−0.9143	0.8432	−0.5186
0.1524	−0.3543	0.5193	−0.9137	0.9035	−0.3501
0.1867	−0.4517	0.6382	−0.8936	0.9483	−0.1528
0.2298	−0.5193	0.6767	−0.8284	1.0000	0.0000
0.3128	−0.7268				
			308.15 K		
0.0000	0.0000	0.2769	−0.6136	0.8103	-1.0500
0.0493	−0.1346	0.3708	−0.7386	0.8432	-1.0086
0.0999	−0.2584	0.4036	−0.8173	0.9035	−0.8137
0.1524	−0.4098	0.5193	−0.9361	0.9483	−0.5582
0.1867	−0.4723	0.5704	−0.9783	1.0000	0.0000
0.2298	−0.5672	0.6767	-1.0780		
			318.15		
0.0000	0.0000	0.3708	-1.1352	0.7589	−0.9387
0.0493	−0.1785	0.4036	-1.2213	0.8103	−0.8172
0.0999	−0.3572	0.5193	-1.3120	0.8432	−0.6343
0.1524	−0.5126	0.5704	-1.3018	0.9035	−0.4673
0.2298	−0.7765	0.6382	-1.2319	0.9483	−0.2076
0.3128	-1.0187	0.6767	-1.1432	1.0000	0.0000

with temperature and not with concentration. From Table 1, it is observed that, at each temperature, the value of ν_{12} is less than that of ν_{21}; i.e., the magnitude of the interaction term of PC–PC–DME is much more than magnitude of the interaction term of DME–DME–PC at all the temperatures. Further, the values of ν_{ij} and ν_{ji} decrease with the increase of temperature. Thus, with the rise of temperature, the three-body interactions of all types become weaker.

Figure 1 shows that the viscosity of the mixture (η) increases gradually with an increase in the PC content in the mixture. The absence of any maxima in the intermediate composition gives an indication of the possible absence of a specific interaction between PC and DME molecules.

From Figure 2, we see that V_m^E values are negative over the entire composition range and become more negative as the temperature increases. The minimum lies at a mole fraction of about 0.5. Studies on the dielectric and spectroscopic properties of propylene carbonate indicate that it behaves as a normal polar liquid with strong dipole–dipole interactions with little or no specific association present (*18*) in it. DME is also a nonassociated solvent (*14*). In the mixture containing propylene carbonate and 1,2-dimethoxyethane, one of the effects which may contribute to V_m^E is the disruption of the intermolecular dipolar forces in propylene carbonate. Since V_m^E values for the mixtures are negative, it appears that the intermolecular interactions between unlike molecules predominate over the intermolecular interactions between like molecules. Considering the molar volumes of PC and DME molecules (85.16 and 104.63 cm^3·mol^{-1}, respectively), it appears that the interstitial accommodation of one component into the structure of the other is not favorable

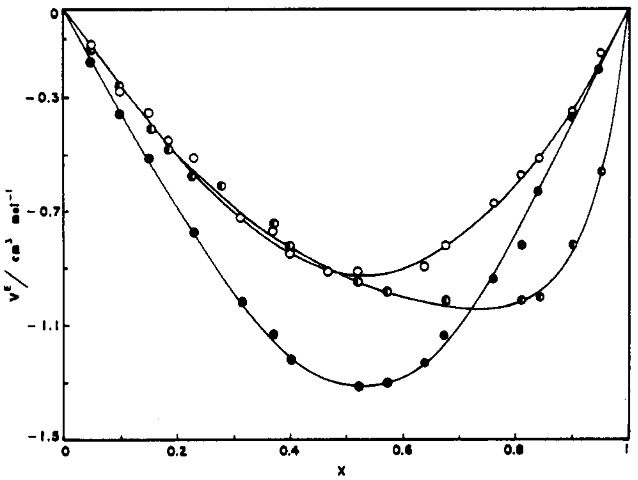

Figure 2. V_m^E for x DME + $(1 - x)$ PC: ○, 298.15 K; ◐, 308.15 K; ●, 318.15 K.

Table 3. Coefficients A_j of Eq 3 and the Standard Deviations σ^E

temp/K	A_0	A_1	A_2	A_3	A_4	σ^E/ (cm^3·mol^{-1})
298.15	-3.6259	0.9344	0.3058	-0.6430	0.5591	0.026
308.15	-3.6537	1.6564	-2.6306	3.7041	-2.0226	0.022
318.15	-5.1634	1.0595	0.7986	-0.7305	0.5523	0.026

enough and so might not have any contribution toward the negative V_m^E values. Thus, it may be concluded that dipolar and dispersion forces between unlike molecules are primarily responsible for negative V_m^E values in PC + DME mixtures.

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