Density and Viscosity of Propylene Carbonate + 2-Methoxyethanol at 298.15, 308.15, and 318.15 K

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Density and viscosity have been measured over the entire composition range for the binary mixtures of propylene carbonate and 2-methoxyethanol at 298.15, 308.15, and 318.15 K. From the experimental results, the excess molar volume (V_m^E) and deviation of viscosity based on the mole fraction average ($\Delta\eta$) have been derived. Kinematic as well as relative viscosity data have also been analyzed by two different methods in terms of interaction parameters. Results have been explained on the basis of molecular interactions and geometric effects of the components in the mixtures.

Introduction

Density and viscosity are two important physical properties of solvent systems and are often used to explain the medium effects of solvents on transport phenomena, electrolyte behavior, and reaction mechanisms that occur in solution. Recent years have thus witnessed a considerable interest in these properties along with the thermodynamic excess functions of binary liquid mixtures (*1–5*). Knowledge of these properties is also helpful to obtain information on the intermolecular interactions for the systems themselves. The potential use of 4-methyl-1,3-dioxolan-2-one more commonly known as propylene carbonate (PC) for a variety of applications particularly in high-energy batteries is well known (*6–8*). 2-Methoxyethanol (methyl cellosolve, ME) also finds a wide range of applications (*9*, *10*) in various electrochemical studies of technological importance. However, few (*11*, *12*) of the binary liquid systems of propylene carbonate with other nonaqueous solvents of practical importance have been studied. In the present study, density and viscosity have been measured for propylene carbonate + 2-methoxyethanol mixtures over the entire composition range at 298.15, 308.15, and 318.15 K, and the results have been discussed.

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 nitrogen gas pressure, the middle fraction being taken each time. The purified sample had a density of 1198.83 kg·m^{-3} and a viscosity of 2.4711 mPa·s at 298.15 K. These values are in good agreement with the literature values 1199.3 kg·m^{-3} (*13*) and 2.480 mPa·s (14).

2-Methoxyethanol (G.R., E. Merck) was distilled three times in an all glass distillation apparatus as described previously (*10*). The density and viscosity of the purified solvent are 960.02 kg·m^{-3} and 1.5414 mPa·s, respectively, and the values compared well with the literature values which are 960.16 kg·m^{-3} (*15*) and 1.5430 mPa·s (*16*) at 298.15 K.

Solvent mixtures were prepared by mixing the appropriate volumes in glass-stoppered air-tight bottles and weighed in a single-pan Mettler balance (Switzerland, model H20) to an accuracy of ±0.000 01 g.

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 was controlled to ±0.01 K. A 60 W heating element and a toluene–mercury thermoregulator were used to maintain the temperature of the experimental thermostat which was placed in a hot cum cold thermostat. The temperature of the hot cum cold thermostat was preset at the desired temperature using a contact thermometer (Jumo, Germany) and an electronic relay system. The absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge. The reproducibility of the density measurement was $\pm 3 \times 10^{-2}$ kg·m^{-3}.

The kinematic viscosities were measured using a suspended Ubbelohde type viscometer. The time of efflux was measured with a stopwatch capable of recording 0.1 s. The viscometer was always kept in a vertical position in a water thermostat controlled to ±0.01 K. The efflux time for water at 298.15 K was about 500 s. The viscometer needed no correction for kinetic energy. The kinematic viscosity (ν) and absolute viscosity (η) are given by the following equations:

$$\nu = Ct - K/t \qquad (1)$$

$$\eta = \nu\varrho \qquad (2)$$

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 using density and viscosity values of water (*17*) and benzene (*18*), were found to be 1.648×10^{-5} cm^2·s^{-2} and −0.023 316 47 cm^2, respectively. The accuracy of the viscosity measurement was ±0.05%.

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

Results

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

The plots of viscosity (η) against the mole fraction of 2-Methoxyethanol are given in Figure 1.

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Table 1. Density (ϱ), Absolute Viscosity (η), Excess Molar Volume (V_m^E), Viscosity Deviation ($\Delta\eta$), and McAllister Interaction Parameter (ν_{ij}) in x 2-Methoxyethanol + (1 − x) Propylene Carbonate

x	ϱ/(kg·m^{-3})	η/(mPa·s)	$10^6 V_m^E$/(m^3·mol^{-1})	$\Delta\eta$/(mPa·s)	x	ϱ/(kg·m^{-3})	η/(mPa·s)	$10^6 V_m^E$/(m^3·mol^{-1})	$\Delta\eta$/(mPa·s)
				T = 298.15 K					
0.0000	1198.83	2.4711	0.000	0.000	0.4979	1085.66	1.7169	−0.110	−0.291
0.0632	1185.41	2.2977	−0.049	−0.115	0.5531	1072.27	1.6801	−0.098	−0.277
0.1045	1176.20	2.1934	−0.055	−0.181	0.5954	1061.74	1.6640	−0.073	−0.254
0.1523	1164.89	2.1038	−0.020	−0.226	0.6954	1035.76	1.6195	0.053	−0.205
0.2117	1149.59	2.0037	0.108	−0.271	0.7346	1025.71	1.5934	0.086	−0.195
0.2527	1140.46	1.9499	0.088	−0.286	0.7959	1010.37	1.5742	0.098	−0.157
0.3050	1130.21	1.8902	−0.047	−0.297	0.8414	999.02	1.5686	0.098	−0.120
0.3489	1120.38	1.8425	−0.076	−0.304	0.9025	983.76	1.5451	0.089	−0.087
0.3970	1109.35	1.7938	−0.094	−0.308	0.9593	969.85	1.5460	0.048	−0.033
0.4547	1095.91	1.7450	−0.108	−0.303	1.0000	960.02	1.5414	0.000	0.000
				$\nu_{12} = 1.5363$, $\nu_{21} = 1.4861$					
				T = 308.15 K					
0.0000	1189.70	2.0476	0.000	0.000	0.4979	1072.18	1.4296	−0.009	−0.225
0.0632	1176.26	1.9134	−0.037	−0.084	0.5954	1052.60	1.3851	0.052	−0.192
0.1045	1167.22	1.8241	−0.046	−0.141	0.6388	1041.82	1.3610	0.081	−0.182
0.1523	1156.30	1.7563	−0.030	−0.171	0.6954	1027.64	1.3413	0.121	−0.157
0.2117	1142.07	1.6786	0.033	−0.202	0.7346	1017.70	1.3247	0.154	−0.143
0.2527	1132.56	1.6341	0.048	−0.214	0.7959	1002.34	1.3099	0.180	−0.109
0.3050	1120.61	1.5811	0.049	−0.226	0.8414	990.98	1.2966	0.194	−0.087
0.3489	1110.68	1.5370	0.037	−0.235	0.9025	975.70	1.2760	0.201	−0.059
0.3970	1099.80	1.4925	0.017	−0.242	0.9593	962.28	1.2659	0.132	−0.024
0.4547	1086.61	1.4559	−0.004	−0.233	1.0000	953.56	1.2579	0.000	0.000
				$\nu_{12} = 1.3027$, $\nu_{21} = 1.2591$					
				T = 318.15 K					
0.0000	1177.96	1.7234	0.000	0.000	0.5531	1054.23	1.1834	0.032	−0.167
0.0632	1164.85	1.6123	−0.036	−0.069	0.5954	1043.69	1.1716	0.086	−0.151
0.1045	1156.26	1.5409	−0.063	−0.112	0.6388	1032.95	1.1466	0.131	−0.146
0.1523	1146.14	1.4840	−0.086	−0.137	0.6954	1018.78	1.1273	0.196	−0.127
0.2117	1133.23	1.4230	−0.097	−0.158	0.7346	1008.83	1.1110	0.2476	−0.1173
0.2527	1124.41	1.3813	−0.116	−0.172	0.7959	993.59	1.0976	0.2936	−0.0894
0.3050	1112.52	1.3389	−0.100	−0.179	0.8414	982.36	1.0825	0.314	−0.074
0.3489	1102.61	1.3065	−0.096	−0.182	0.9025	967.43	1.0760	0.319	−0.039
0.3970	1091.56	1.2729	−0.084	−0.183	0.9593	954.18	1.0554	0.259	−0.021
0.4547	1077.99	1.2237	−0.052	−0.180	1.0000	947.15	1.0494	0.000	0.000
0.4979	1067.69	1.2142	−0.022	−0.174					
				$\nu_{12} = 1.1087$, $\nu_{21} = 1.0808$					

Table 2. Coefficients A_j of Eq 6 for V_m^E and the Standard Deviations $\sigma(V_m^E)$ at 208.15. 308.15, and 318.15 K

T/K	A_0	A_1	A_2	A_3	A_4	$10^6\sigma(V_m^E)$/(cm^3·mol^{-1})
298.15	−0.4593	0.2245	4.0510	−1.8413	−4.3483	0.039
308.15	0.0944	0.0327	1.5310	−2.7296	−0.2745	0.020
318.15	0.0465	−1.1076	−0.2040	−2.9147	4.3610	0.031

The kinematic viscosity data have been analyzed by means of the McAllister equation (*19*):

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

where x is the mole fraction of 2-methoxyethanol, ν_1, ν_2, and ν are the respective kinematic viscosities of 2-methoxyethanol, propylene carbonate, and their mixtures, and M_1 and M_2 are the molecular weights of 2-methoxyethanol and propylene carbonate, respectively. The interaction parameters, ν_{ij}, at different temperatures are also reported in Table 1.

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

$$V_m^E = [xM_1 + (1 - x)M_2]/\varrho - xM_1/\varrho_1 - (1 - x)M_2/\varrho_2 \quad (4)$$

where ϱ_1, ϱ_2, and ϱ are the densities of 2-methoxyethanol, propylene carbonaote, and their binary mixtures, respectively, and other terms have their significance as mentioned above. The excess molar volumes have been presented in Table 1.

The deviation of viscosity from the mole fraction average ($\Delta\eta$) has been calculated from the equation

$$\Delta\eta = \eta - [x\eta_1 + (1 - x)\eta_2] \quad (5)$$

and the values have been reported in Table 1.

The plots of V_m^E against the mole fraction (x) of 2-methoxyethanol are given in Figure 2. The excess molar volume was fitted to the Redlich–Kister equation (*20*):

$$V_m^E/(\text{m}^3\cdot\text{mol}^{-1}) = x(1 - x)\sum_{j=0}^{n} A_j(2x - 1)^j \quad (6)$$

where A_0, A_1, A_2, etc. are adjustable parameters. These parameters were calculated by the method of least squares. The values of these parameters along with the standard deviations $\sigma(V_m^E)$ as defined by

$$\sigma(V_m^E) = \left[\frac{\sum(V_{m,\text{exptl}}^E - V_{m,\text{calcd}}^E)^2}{(N - M)}\right]^{0.5} \quad (7)$$

are recorded in Table 2. In eq 7, N is the total number of

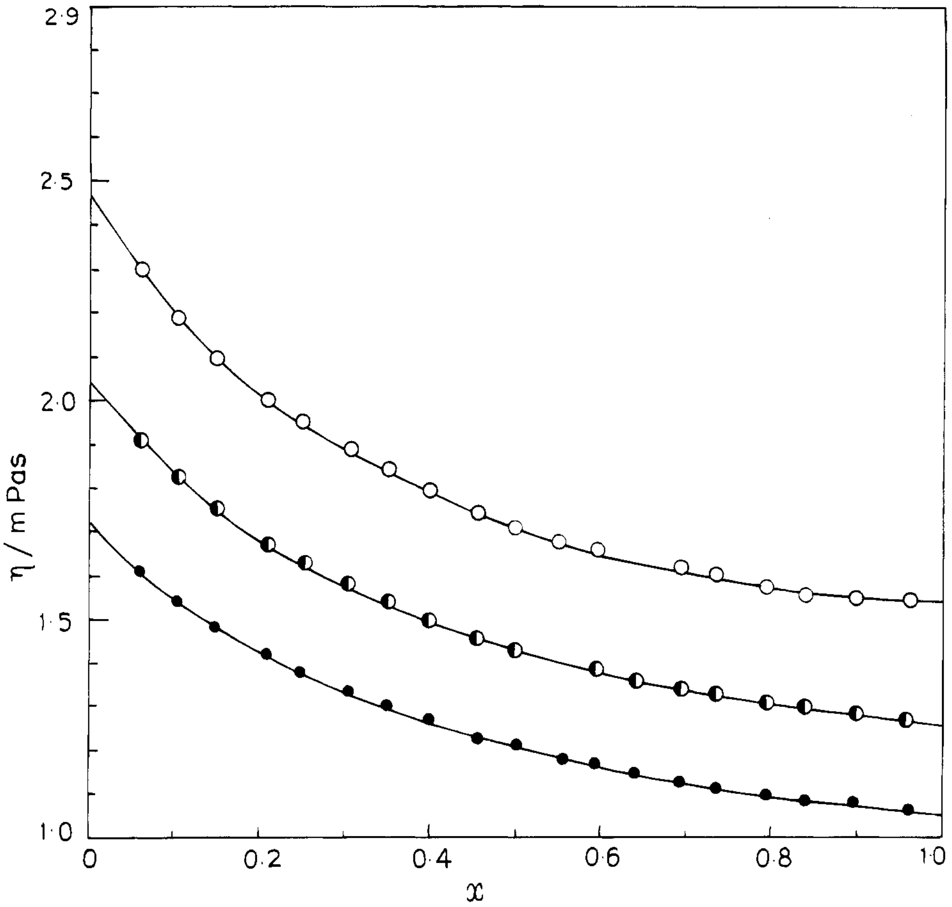

Figure 1. Viscosities (η) for the binary mixtures of x 2-methoxyethanol + $(1 - x)$ propylene carbonate at 298.15 (○), 308.15 (◐), and 318.15 K (●).

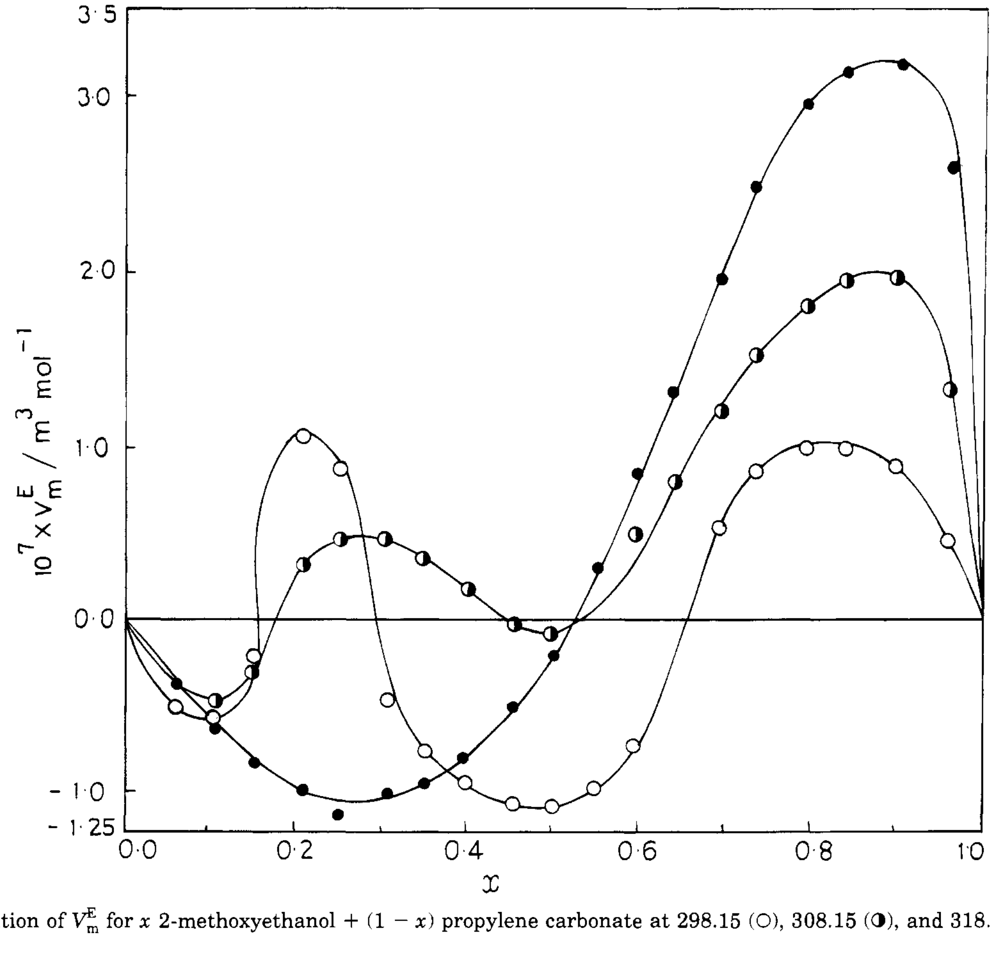

Figure 2. Variation of V_m^E for x 2-methoxyethanol + $(1 - x)$ propylene carbonate at 298.15 (○), 308.15 (◑), and 318.15 K (●).

experimental points and M is the number of adjustable parameters.

Discussion

From Table 1, we see that the density as well as viscosity of the binary liquid mixture decreases monotonically with an increase in the 2-methoxyethanol content in the mixture at all three studied temperatures.

In the interaction parameter ν_{ij}, values of ν_{ij} can change with temperature but not with concentration. Table 1 shows that the values of ν_{12} are very close to the corresponding ν_{21} values at the respective temperature, and it indicates that the magnitude of the interaction term of the ME–ME–PC type is almost equal to that arising from PC–PC–ME type interactions. Further, the values of ν_{12} and ν_{21} decrease with increasing temperature. Thus, with a 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 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 2-methoxyethanol molecules (*21*).

From Figure 2, we see that the sign of the $V_{\mathrm{m}}^{\mathrm{E}}$ values changes in some unsymmetric fashion with the change in mole fraction of the constituents in the mixture. However, with a rise of temperature from 298.15 to 318.15 K, the changes in sign of $V_{\mathrm{m}}^{\mathrm{E}}$ values become less frequent. The unsymmetrical nature of $V_{\mathrm{m}}^{\mathrm{E}}$ vs mole fraction curves in the binary system appears to be primarily due to steric factors arising from a change in the proportion of different geometric forms of 2-methoxyethanol molecules with a change in its mole fraction. Similar unsymmetrical variation of $V_{\mathrm{m}}^{\mathrm{E}}$ has been observed for tetrahydrofuran + *p*-dioxane binary systems (*22*).

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