Excess Molar Volumes, Viscosities, and Refractive Indices of Triethylene Glycol Dimethyl Ether with Dimethyl Carbonate, Diethyl Carbonate, and Propylene Carbonate at 298.15 K

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Excess molar volumes viscosities, and refractive indices for mixtures of triethylene glycol dimethyl ether with dimethyl carbonate, diethyl carbonate, or propylene carbonate have been measured over the concentration range at 298.15 K and at atmospheric pressure. Excess volume data have been correlated using the Redlich−Kister polynomial equation by the method of least squares for the estimation of the adjustable parameters and the standard errors. The experimental results have been qualitatively discussed.

Introduction

In our previous paper (Pal and Kumar, 1997), we studied the excess molar volumes, viscosities, and refractive indices of binary mixtures of diethylene glycol dimethyl ether with esters of carbonic acid at atmospheric pressure and at 298.15 K. In continuation of these investigations on the thermodynamic and transport properties of some mixtures of polyethers with organic solvents (Pal and Sharma, 1998a,b), the present paper reports the excess molar volumes, V_m^E, viscosities, η, and refractive indices, n_D, for mixtures containing triethylene glycol dimethyl ether (tri-EGDME) with dimethyI carbonate (DMC), diethyl carbonate (DEC), or propylene carbonate (PC) over the mole-fraction range at 298.15 K and at atmospheric pressure. Excess properties of binary mixtures containing esters of carbonic acid have previously been studied by several authors (Barthel et al., 1995; Francesconi and Comelli, 1997a; Comelli and Francesconi, 1997; Moumouzias and Ritzoulis, 1997). The present study was therefore undertaken in order to compare the excess molar volumes, viscosities, and refractive indices of triethylene glycol dimethyl ether + esters of carbonic acid with those of our previous results for diethylene glycol dimethyl ether + esters of carbonic acid (Pal and Kumar, 1997) by the addition of an OC_2H_4 unit, for species with a common alkyl chain.

Experimental Section

Materials. Dimethyl carbonate (Spectrochem, Bombay; >98.8 mass %), diethyl carbonate (Spectroschem, Bombay; >99 mass %), and propylene carbonate (Mark-Schuchardt >99 mass %) were the same as those used in earlier studies (Pal and Kumar, 1997). Triethylene glycol dimethyl ether (Acros, U.S.; >99 mass %) was fractionally distilled with sodium under reduced nitrogen gas pressure, and only the middle fraction was collected. Karl-Fischer titration gave water contents of <0.01 mass %. The densities, viscosities, and refractive indices of these liquids are compared with their corresponding literature values in Table 1. All liquids were kept in dark bottles over molecular sieves (Fluka, AG) to reduce the water content. Before use, all liquids were partially degassed under vacuum.

Table 1. Densities (ρ), Viscosities (η), and Refractive Indices (n_D) of Pure Liquids and Comparison with Literature Values at 298.15 K

	ρ/g·cm^{-3}		η/mPa·s		n_D	
liquid	exptl	lit.	exptl	lit.	exptl	lit.
triethylene glycol dimethyl ether	0.9807	0.979 5[a] 0.980 67[b] 0.980 01[c]	1.950	1.96[a]	1.4239	1.4209[a]
dimethyl carbonate	1.0632	1.063 28[d] 1.063 60[e] 1.063 33[f]	0.589		1.3710	1.3667[d]
diethyl carbonate	0.9690	0.969 23[g] 0.969 26[h]	0.749		1.3859	1.3827[g]
propylene carbonate	1.1988	1.198 83[i] 1.197 8[j] 1.199 2[l]	2.493	2.4711[i] 2.51[k]	1.4210	1.4194[j]

[a] Wallace et al. (1968). [b] Tovar et al. (1997). [c] Treszszanowicz et al. (1990). [d] Francesconi and Comelli (1996). [e] Garcia et al. 1988. [f] Comelli et al. (1997). [g] Francesconi and Comelli (1997a). [h] Riddick et al. (1986). [i] Muhuri and Hazra (1995). [j] Moumouzias and Ritzoulis (1997). [k] Barthel et al. (1995). [l] Wilhelm et al. (1991).

Apparatus and Procedure. The excess molar volumes were measured in a dilution dilatometer in similar fashion to that described by Dickinson et al. (1975). Details of its calibration, experimental setup, and operational procedure have been described elsewhere (Pal and Singh, 1994). The mercury meniscus, as well as the reference mark, were measured with the help of a cathetometer that could read correctly to within 0.01 mm. Before the experimental measurements, the mixture benzene + cyclohexane was used to check the dilatometer. The excess molar volumes are reproducible to ±0.003 cm^3·mol^{-1} (Pal and Singh, 1994). The composition of each mixture was obtained with an accuracy of 1×10^{-4} from the measured apparent masses of the components. All the mass measurements were performed on an electronic balance (Dhona 200D, India) accurate to ±0.01 mg. All masses were corrected for buoyancy. All molar quantities was based on the relative atomic mass table of 1986 issued by IUPAC (1986). Each run covered just over half of the mole fraction range so as to give an overlap between two runs.

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Table 2. Excess Molar Volumes (V_m^E) for Binary Mixtures at 298.15 K

x_1	V_m^E/cm^3·mol^{-1}	x_1	V_m^E/cm^3·mol^{-1}	x_1	V_m^E/cm^3·mol^{-1}	x_1	V_m^E/cm^3·mol^{-1}
Triethylene G1ycol Dimethyl Ether (1) + Dimethyl Carbonate (2)							
0.0236	−0.002	0.2067	−0.017	0.4467	−0.044	0.7334	−0.039
0.0500	−0.003	0.2243	−0.020	0.4845	−0.046	0.7013	−0.034
0.0658	−0.004	0.2562	−0.024	0.5320	−0.047	0.8623	−0.023
0.0933	−0.007	0.2982	−0.028	0.5773	−0.048	0.9267	−0.013
0.1165	−0.009	0.3417	−0.031	0.6400	−0.045		
0.1667	−0.016	0.4014	−0.038	0.6909	−0.043		
Triethylene Glycol Dimethyl Ether (1) + Diethyl Carbonate (2)							
0.0271	−0.014	0.2992	−0.083	0.4334	−0.095	0.7260	−0.069
0.0633	−0.027	0.3275	−0.086	0.4631	−0.096	0.7822	−0.060
0.1186	−0.044	0.3438	−0.080	0.5128	−0.093	0.8667	−0.041
0.1790	−0.059	0.3645	−0.090	0.5712	−0.087	0.9155	−0.020
0.2379	−0.071	0.3958	−0.092	0.6267	0.083		
0.2692	−0.076	0.4106	−0.093	0.6699	−0.078		
Triethylene Glycol Dimethyl Ether (1) + Propylene Carbonate (2)							
0.0146	−0.036	0.2251	0.439	0.3866	−0.616	0.8173	−0.388
0.0396	−0.090	0.2471	−0.469	0.4218	−0.636	0.8692	−0.296
0.0733	−0.157	0.2781	−0.511	0.4790	−0.649	0.9260	−0.184
0.0931	−0.197	0.2962	−0.527	0.5504	−0.639	0.9155	−0.020
0.1370	−0.285	0.3113	−0.550	0.6206	−0.608		
0.1915	−0.382	0.3461	−0.583	0.7451	−0.492		

Table 3. Values of the Parameters of Eq 2 and Standard Deviation $s(V_m^E)$ at 298.15 K

	a_0	a_1	a_2	a_3	$s(V_m^E)$/cm^3·mol^{-1}
triethylene glycol dimethyl ether (1) + dimethyl carbonate (2)	0.182	-0.090	0.077	0.042	0.001
triethylene glycol dimethyl ether (1) + diethyl carbonate (2)	−0.374	−0.047	0.006	0.030	0.002
triethylene glycol dimethyl ether (1) + propylene carbonate (2)	−2.596	0.010	0.160	−0.278	0.003

Table 4. Densities (ρ) and Viscosities (η) for Binary Mixture at 298.15 K

x_1	ρ/g·cm^{-3}	η/mPa·s	x_1	ρ/g·cm^{-3}	η/mPa·s	x_1	ρ/g·cm^{-3}	η/mPa·s
Triethylene Glycol Dimethyl Ether (1) + Dimethyl Carbonate (2)								
0.0000	1.0632	0.589	0.2147	1.0329	0.888	0.6515	0.9975	1.524
0.0029	1.0627	0.592	0.2593	1.0280	0.953	0.6923	0.9951	1.585
0.0133	1.0609	0.606	0.3084	1.0231	1.026	0.7622	0.9914	1.673
0.0209	1.0596	0.618	0.3099	1.0230	1.025	0.8150	0.9888	1.740
0.0436	1.0559	0.651	0.3614	1.0183	1.099	0.8324	0.9879	1.760
0.0642	1.0526	0.679	0.4011	1.0149	1.157	0.9158	0.9842	1.860
0.0947	1.0482	0.721	0.4433	1.0115	1.221	0.9541	0.9825	1.899
0.1187	1.0448	0.753	0.5005	1.0072	1.303	1.0000	0.9807	1.950
0.1459	1.0412	0.792	0.5659	1.0029	1.396			
0.1856	1.0363	0.846	0.6004	1.0006	1.449			
Triethylene Glycol Dimethyl Ether (1) + Diethyl Carbonate (2)								
0.0000	0.9690	0.749	0.1983	0.9726	0.966	0.6561	0.9781	1.519
0.0103	0.9692	0.759	0.2499	0.9734	1.021	0.7044	0.9786	1.583
0.0175	0.9694	0.767	0.3024	0.9742	l.081	0.7371	0.9788	1.624
0.0246	0.9695	0.775	0.3233	0.9745	1.105	0.7905	0.9793	1.693
0.0367	0.9697	0.788	0.3543	0.9749	1.142	0.8464	0.9797	1.764
0.0576	0.9702	0.813	0.4034	0.9743	1.199	0.9175	0.9802	1.850
0.0367	0.9697	0.708	0.3543	0.9749	1.142	0.3464	0.9797	1.764
0.0576	0.9702	0.813	0.4034	0.9743	1.199	0.9175	0.9802	1.850
0.0787	0.9706	0.837	0.4614	0.9762	1.268	0.9510	0.9804	1.894
0.0958	0.9709	0.856	0.5022	0.9766	1.324	1.0000	0.9807	1.950
0.1190	0.9713	0.879	0.5520	0.9771	1.386			
0.1509	O.9718	0.9l3	0.6112	0.9777	1.463			
Triethylene Glycol Dimethyl Ether (1) + Propylene Carbonate (2)								
0.0000	1.1988	2.493	0.2559	1.1114	2.561	0.6786	1.0241	2.254
0.0049	1.1967	2.492	0.3083	1.0977	2.543	0.7038	1.0202	2.227
0.0113	1.1940	2.496	0.3356	1.0910	2.539	0.8165	1.0039	2.127
0.0249	1.1883	2.504	0.3930	1.0777	2.494	0.8598	0.9980	2.088
0.0352	1.1841	2.516	0.4660	1.0622	2.444	0.8959	0.9934	2.047
0.0525	1.1772	2.523	0.4902	1.0573	2.428	0.9347	0.9885	2.021
0.0833	1.1656	2.536	0.5272	0.0502	2.402	0.9640	0.9850	1.990
0.1358	1.1473	2.560	0.5728	1.0419	2.361	1.0000	0.9807	1.950
0.1928	1.1294	2.568	0.6242	1.0330	2.308			

The kinematic viscosities of the pure liquids and the mixtures were measured at atmospheric pressure and at 298.15 K using an Ubbelohde suspended-level viscosmeter. The viscometer was calibrated with thrice-distilled water and twice-distilled benzene at the working temperature. Care was taken to reduce evaporation during the measurements. The average of four or five sets of flow times for each fluid was taken for the purpose of the calculation of viscosity. The flow-time measurements were made with an electronic stopwatch having a precision of ±0.01 s. The measured values of the kinematic viscosties were converted to dynamic viscosity, η, after multiplication by the density.

Table 5. Refractive Indices (n_D) for Binary Mixtures at 298.15 K

x_1	n_D	x_1	n_D	x_1	n_D
Triethylene Glycol Dimethyl Ether (1) + Dimethyl Carbonate (2)					
0.0000	1.3710	0.4003	1.4019	0.8307	1.4201
0.0285	1.3737	0.5584	1.4091	0.8769	1.4206
0.0563	1.3763	0.6648	1.4144	0.9395	1.4219
0.1361	1.3845	0.7118	1.4161	0.9580	1.4224
0.2111	1.3899	0.7875	1.4178	0.9766	1.4228
0.3309	1.3980	0.8137	1.4197	1.0000	1.4239
Triethylene Glycol Dimethyl Ether (1) + Diethyl Carbonate (2)					
0.0000	1.3859	0.3614	1.4033	0.8954	1.4207
0.0117	1.3862	0.4512	1.4070	0.9220	1.4211
0.0924	1.3908	0.5658	1.4109	0.9753	1.4231
0.1423	1.3935	0.6598	1.4139	1.0000	1.4239
0.1963	1.3960	0.7577	1.4177		
0.2475	1.3979	0.8436	1.4198		
Triethylene Glycol Dimethyl Ether (1) + Propylene Carbonate (2)					
0.0000	1.4221	0.2244	1.4242	0.7450	1.4243
0.0040	1.4222	0.3632	1.4246	0.8842	1.4243
0.0442	1.4226	0.4140	1.4251	0.9348	1.4241
0.0936	1.4231	0.4601	1.4251	0.9688	1.4240
0.1141	1.4233	0.5560	1.4248	1.0000	1.4239
0.1862	1.4240	0.6896	1.4246		

The values of η thus obtained were reproducible to ±0.003 mPa·s. The performance of the viscometer was checked by measuring and comparing the viscosities of the pure liquids with the value reported in the literature (Riddick et al., 1986). Densities of pure liquids were measured using double-armed pycnometer with an accuracy of 5 parts in 10^5. A thermostatically controlled, well-stirred water bath whose temperature was controlled to ±0.01 K was used for all the measurements. Densities of the liquid mixtures were computed from the excess molar volume (V_m^E) and composition according to the equation

$$\rho = \frac{x_1M_1 + x_2M_2}{V_m^E + V^\circ} \tag{1}$$

where x_1 and x_2 are the mole fractions and M_1 and M_2 represent molar masses of components 1 and 2, respectively. V° stands for ideal molar volume.

Refractive indices, n_D, were measured with a separate set of solutions at (298.15 ±0.01) K and atmospheric pressure with a Baush and Lomb Abbe 3L refractometer. Calibration of the apparatus and working procedure have been described in our previous paper (Pal and Kumar, 1997). An average of triplicate measurements was considered for the calculation of refractive index values. Readings were reproducible within ±0.0001 units.

Results and Discussion

The experimental excess molar volumes, viscosities, and refractive indices of the different binary mixtures at 298.15 K and at various mole fractions are reported in Tables 2, 4, and 5.

The plots of V_m^E against the mole fraction (x_1) of ether are given in Figure 1. The excess molar volumes for all mixtures were fitted to the Redlich−Kister polynomial

$$V_m^E/\mathrm{cm^3\cdot mol^{-1}} = x_1x_2\sum_{j=0}^{k} a_j(x_2 - x_1)^j \tag{2}$$

where a_j is the polynomial coefficient and k is the polynomial degree. The values of the coefficients a_j were evaluated by the method of least squares with all points weighted equally and are summarized in Table 3 along with the standard deviations $s(V_m^E)$. For all mixtures, $s(V_m^E) \leq 0.003$ cm^3·mol^{-1}, showing the good accuracy attainable with the dilatometer used.

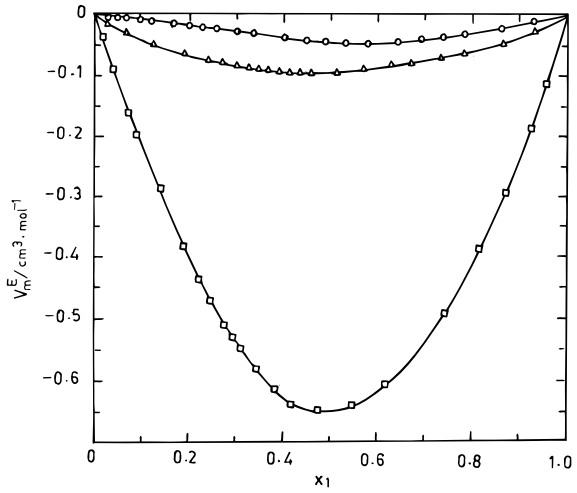

Figure 1. Comparison of the excess. molar volume (V_m^E) of different mixtures at 298.15 K: (○) dimethyl carbonate, (△) diethyl carbonate, and (□) propylene carbonate.

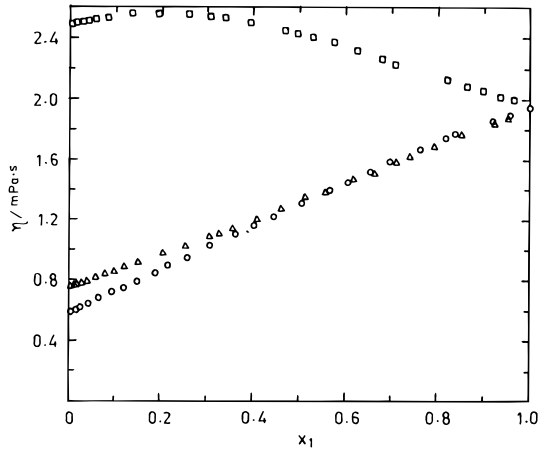

Figure 2. Comparison of the dynamic viscosity (η) of different mixtures at 298.15 K: (○) dimethyl carbonate, (△) diethyl carbonate, and (□) propylene carbonate.

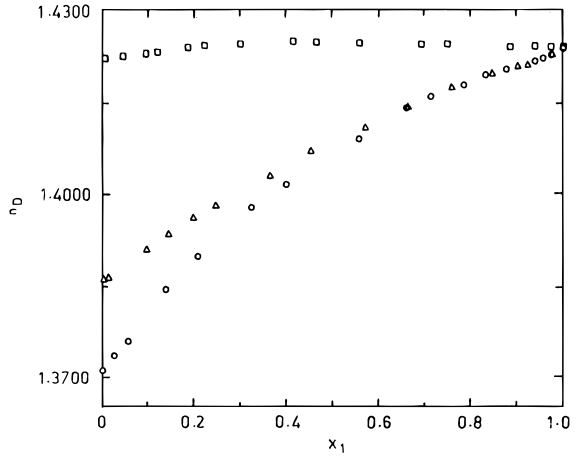

Figure 3. Comparison of the refractive index (η_D) of different mixtures at 298.15 K: (○) dimethyl carbonate, (△) diethyl carbonate, and (□) propylene carbonate.

Table 2 and Figure 1 show that the excess volume are negative for all mixtures over the entire composition range. The behavior is similar for a diethylene glycol dimethyl ether (Pal and Kumar, 1997) but with a marked decrease in V_m^E here. The value of V_m^E decreases and becomes a symmetrical function of x_1 as the chain length of the hydrophilic moiety $-OC_2H_4-$ increases. The negative values of V_m^E for all the three mixtures show the specific but complex pattern for the interactions between molecules. Among the several factors and balancing forces, the dipole−dipole interactions within the molecules are dominating in all mixtures. It is important to note that a considerable amount of volume contraction is observed for the triglyme with propylene carbonate mixtures. This contrasts with the behavior of the H_m^E and V_m^E for the esters of carbonic acid either with higher alkanols, alkoxyethanol, or alkyl acetate (Francesconi and Comelli, 1997a; Comelli and Francesconi, 1997; Muhuri and Hazra, 1995; Comelli et al., 1997) but consistent with that of the V_m^E for the dialkyl carbonates with branched ether (Francesconi and Comelli, 1997b).

The dependence of η and n_D on the mole fraction of triglyme for all the three mixtures at 298.15 K is displayed in Figures 2 and 3 wherein we observe that η and n_D for different components of the mixtures vary in the sequence dimethyl carbonate < diethyl carbonate < propylene carbonate. Figures 2 and 3 show that the dynamic viscosity as well as refractive index of the binary liquid mixtures of dimethyl carbonate and diethyl carbonate with triglyme increases whereas for the mixture with propylene carbonate it shows maxima in the region $0.2 < x_1 < 0.3$, being increases at lower values of x_1 and decreases for higher values of x_1.

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