Articles

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

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Excess molar volumes, V_m^E viscosities, η, and refractive indices, n_D, have been measured for the binary mixtures tetraethylene glycol dimethyl ether + dimethyl carbonate, + diethyl carbonate, and + propylene carbonate at 298.15 K and at atmospheric pressure over the complete composition range. The results are compared with those of previous investigations for binary mixtures containing esters of carbonic acid.

Introduction

This paper is part of our systematic program of research on the measurement of transport properties (Pal and Kumar, 1998; Pal et al., 1998) of binary liquid mixtures containing esters of carbonic acid widely used as industrial solvents.

In this communication we report on the measured values of excess molar volumes, viscosities, and refractive indices, at 298.15 K and at atmospheric pressure, of binary mixtures of tetraethylene glycol dimethyl ether (tetra-EGDME) + dimethyl carbonate (DMC), + diethyl carbonate (DEC), and + propylene carbonate (PC). A perusal of the literature reveals that the thermodynamic properties of binary mixtures of an ester of carbonic acid with either higher alkanols, alkoxyethanol, alkyl acetate, or hydrocarbon (Francesconi and Comelli, 1997a; Muhuri and Hazra 1995; Comelli et al., 1997; Treszczanowicz, 1990) have been studied. A few other studies involving the isobaric vapor−liquid equilibria of dimethyl carbonate + 1,2-epoxybutane (Francesconi and Comelli, 1996) and relative permittivities and refractive indices of propylene carbonate + toluene (Moumnouzias and Ritzoulis, 1997) have also been made. The aim of this work is to provide a set of values for the characterization of the molecular interactions of these mixtures and to examine the effect of the enlargement of the polar head group of the polyether 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 (Spectrochem, Bombay, >99 mass %), and propylene carbonate (Merck-Schuchardt >99 mass %) were the same as used in earlier studies (Pal and Kumar, 1998; Pal et al., 1988). Tetraethylene glycol dimethyl ether (Acros, USA, >99 mass %) was used as received. All samples were kept in tightly sealed bottles to minimize adsorption of atmospheric moisture and CO_2. Before the measurements, all liquids were partially degassed and dried over molecular sives type 4A to reduce water content. 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. Corrections were made for buoyancy. All molar quantities were used in the relative atomic mass table of 1986 issued by IUPAC (1986).

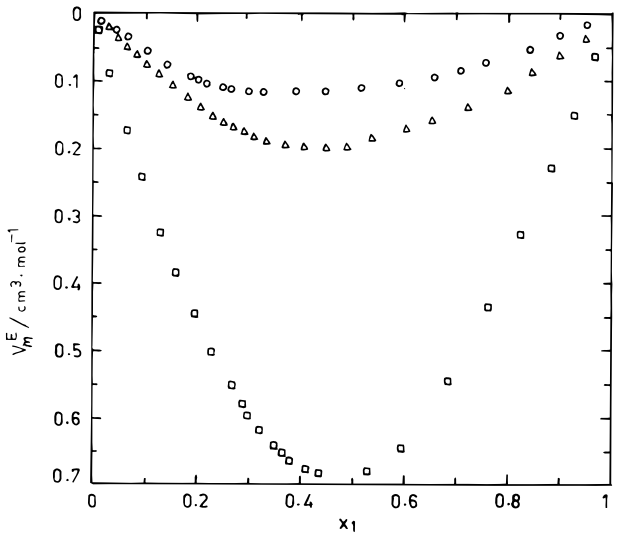

Figure 1. Excess molar volume (V_m^E) of binary mixtures containing tetraethylene glycol dimethyl ether + dimethyl carbonate (○), + diethyl carbonate (△), and + propylene carbonate (□) at 298.15 K.

Apparatus and Procedure. Excess volumes, which are accurate to ±0.003 $cm^3 \cdot mol^{-1}$, 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 previously (Pal and Singh, 1994). The dilatometer was clamped vertically into the water bath. Readings of the reference marks and those of liquid levels filling the dilatometer were measured with a cathetometer having a precision of ±0.001 cm. Each run covered just over half of the mole fraction range so as to give an overlap between two runs.

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10.1021/je9800961 CCC: $18.00
Published on Web 11/06/1998

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

	ρ/g·cm^{-3}		η/mPa·s		n_D	
liquid	exptl	lit.	exptl	lit.	exptl	lit.
tetraethylene glycol dimethyl ether	1.0063	1.006 62[a] 1.006 27[b]	3.394		1.4334	
dimethyl carbonate	1.0632	1.063 30[c] 1.063 33[d] 1.063 28[e]	0.589		1.3710	1.3667[e]
diethyl carbonate	0.9690	0.969 26[f] 0.969 23[g] 0.969 27[c]	0.749		1.3859	1.3827[g]
propylene carbonate	1.1988	1.198 83[h] 1.197 8	2.493	2.4711[h] 2.51[j]	1.4210	1.4194[i]

[a] Treszszanowicz (1990). [b] Defhlefsen and Hvidt (1985). [c] Francesconi and Comelli (1995). [d] Comelli et al. (1997). [e] Francesconi and Comelli (1996). [f] Riddick et al. (1986). [g] Francesconi and Comelli (1997a). [h] Muhuri and Hazra (1995). [i] Moumouzias and Ritzoulis (1997). [j] Barthel et al (1995).

Table 2. Experimental 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}
Tetraethylene Glycol Dimethyl Ether (1) + Dimethyl Carbonate (2)							
0.0096	−0.005	0.1907	−0.091	0.3299	−0.116	0.7080	−0.082
0.0202	−0.010	0.2027	−0.094	0.3901	−0.115	0.7527	−0.069
0.0436	−0.025	0.2166	−0.100	0.4470	−0.117	0.8420	−0.061
0.0670	−0.035	0.2551	−0.106	0.5125	−0.110	0.8979	−0.032
0.1045	−0.056	0.2680	−0.109	0.5881	−0.103	0.9533	−0.017
0.1422	−0.075	0.3005	−0.112	0.6550	−0.092		
Tetraethylene Glycol Dimethyl Ether (1) + Diethyl Carbonate (2)							
0.0213	−0.018	0.1835	−0.127	0.3332	−0.184	0.6519	−0.158
0.0436	−0.037	0.2067	−0.140	0.3706	−0.192	0.7219	−0.137
0.0634	−0.050	0.2337	−0.156	0.4108	−0.196	0.7937	−0.116
0.0806	−0.062	0.2501	−0.162	0.4494	−0.197	0.8490	−0.086
0.1032	−0.078	0.2668	−0.165	0.4902	−0.192	0.9007	−0.061
0.1272	−0.091	0.2940	−0.173	0.5368	−0.184	0.9506	−0.033
0.1534	−0.110	0.3073	−0.183	0.6058	−0.170		
Tetraethylene Glycol Dimethyl Ether (1) + Propylene Carbonate (2)							
0.0072	−0.020	0.2305	−0.503	0.3690	−0.650	0.6826	−0.548
0.0288	−0.087	0.2661	−0.551	0.3783	−0.662	0.7640	−0.434
0.0611	−0.170	0.2893	−0.580	0.4149	−0.675	0.8233	−0.330
0.0941	−0.242	0.2982	−0.593	0.4345	−0.680	0.8819	−0.228
0.1295	−0.325	0.3243	−0.618	0.5267	−0.676	0.9246	−0.150
0.1585	−0.386	0.3542	−0.643	0.5915	−0.645	0.9690	−0.060
0.1596	−0.447						

Table 3. Values of the Parameters of Eq 1 and Standard Deviations σ (V_m^E) at 298.15 K

	a_0	a_1	a_2	a_3	$\sigma(V_m^E)$/ cm^3·mol^{-1}
tetraethylene glycol dimethyl ether (1) + dimethyl carbonate (2)	−0.453	0.197	−0.066	−0.076	0.002
tetraethylene glycol dimnethyl ether (1) + diethyl carbonate (2)	−0.765	0.232	−0.007	−0.224	0.002
tetraethylene glycol dimethyl ether (1) + propylene carbonate (2)	−2.728	0.358	0.347	0.176	0.003

The kinematic viscosities of both the pure components and their mixtures were measured at atmospheric pressure and at 298.15 K by an Ubbelohde suspended-level viscometer, which was calibrated with doubly distilled water and benzene. Care was taken to reduce evaporation during the measurements. The other experimental details have been given previously (Pal and Singh, 1996).

Viscosities are reproducible to ±0.003 mPa·s. Densities of pure liquids were measured with a precalibrated bicapillary pycnometer with an accuracy of 5 parts in 10^5. All the measurements were carried out in a well-stirred water bath whose temperature was controlled to ±0.01 K.

Refractive indices for the sodium D line of the pure components and their binary mixtures were measured at 298.15 K and at atmospheric pressure with a Baush and Lomb Abbe 3L refractometer. Calibration of the apparatus and the working procedure have been described in our previous paper (Pal and Kumar, 1998). The refractive indices were accuate to ±0.0001 unit.

Results and Discussion

Table 1 gives the experimental densities ρ, viscosities η, and refractive indices n_D for the pure liquids, together with some values given in the literature. Tables 2, 4, and 5 report V_m^E, η, and n_D of the different binary mixtures at 298.15 K at various mole fractions.

The excess molar volumes for all the mixtures have been correlated using the Redlich−Kister polynomial

$$V_m^E/\text{cm}^3\cdot\text{mol}^{-1} = x_1x_2\sum_{k=0}^{n} a_k(x_2 - x_1)^k \qquad (1)$$

where x_1, x_2 are the mole fractions of components, a_k are the polynomial coefficients, and n is the polynomial degree.

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

x_1	ρ/g·cm^{-3}	η/m Pa·s	x_1	ρ/g·cm^{-3}	η/m Pa·s	x_1	ρ/g·cm^{-3}	η/m Pa·s
Tetraethylene Glycol Dimethyl Ether (1) + Dimethyl Carbonate (2)								
0.0000	1.0632	0.589	0.1595	1.0452	0.994	0.6174	1.0178	2.382
0.0013	1.0630	0.595	0.2094	1.0408	1.132	0.6892	1.0152	2.606
0.0051	1.0625	0.603	0.3042	1.0338	1.414	0.7492	1.0131	2.781
0.0117	1.0616	0.623	0.3316	1.0320	1.499	0.7839	1.0121	2.888
0.0228	1.0601	0.642	0.3593	1.0303	1.576	0.8643	1.0097	3.113
0.0349	1.0585	0.673	0.3994	1.0280	1.703	0.9142	1.0084	3.237
0.0584	1.0557	0.726	0.4379	1.0259	1.815	0.9490	1.0075	3.324
0.0861	1.0525	0.792	0.4770	1.0239	1.945	0.9732	1.0069	3.369
0.1164	1.04931	0.875	0.5477	1.0207	2.159	1.0000	1.0063	3.394
Tetraethylene Glycol Dimethyl Ether (1) + Diethyl Carbonate (2)								
0.0000	0.9690	0.749	0.2814	0.9856	1.348	0.6910	0.9997	2.478
0.0049	0.9694	0.752	0.3146	0.9871	1.434	0.7376	1.0008	2.614
0.0140	0.9700	0.772	0.3497	0.9886	1.519	0.7849	1.0020	2.760
0.0274	0.9710	0.796	0.3949	0.9904	1.634	0.8377	1.0032	2.915
0.0440	0.9721	0.824	0.4546	0.9926	1.798	0.8758	1.0040	3.028
0.0680	0.9737	0.879	0.5017	0.9942	1.939	0.9345	1.0051	3.218
0.0984	0.9757	0.938	0.5551	0.9959	2.083	0.9719	1.0058	3.328
0.1416	0.9783	1.029	0.5999	0.9972	2.204	0.9868	1.0061	3.378
0.2036	0.9818	1.164	0.6478	0.9985	2.349	1.0000	1.0063	3.394
Tetraethylene Glycol Dimethyl Ether (1) + Propylene Carbonate (2)								
0.0000	1.1988	2.493	0.1537	1.1412	3.083	0.5433	1.0579	3.607
0.0021	1.1978	2.505	0.1752	1.1347	3.145	0.6081	1.0485	3.609
0.0047	1.1967	2.510	0.2194	1.1224	3.268	0.6396	1.0443	3.615
0.0111	1.1938	2.543	0.2590	1.1123	3.355	0.7173	1.0346	3.588
0.0248	1.1878	2.604	0.3006	1.1025	3.428	0.7820	1.0272	3.559
0.0362	1.1830	2.663	0.3585	1.0901	3.506	0.8311	1.0219	3.541
0.0516	1.1768	2.716	0.3967	1.0826	3.560	0.8960	1.0155	3.498
0.0765	1.1672	2.814	0.4451	1.0738	3.590	0.9403	1.0114	3.466
0.1064	1.1566	2.935	0.4956	1.0653	3.602	1.0000	1.0063	3.394

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
Tetraethylene Glycol Dimethyl Ether (1) + Dimethyl Carbonate (2)					
0.0000	1.3710	0.2420	1.4002	0.6158	1.4254
0.0042	1.3725	0.2826	1.4038	0.7190	1.4285
0.0143	1.3737	0.3588	1.4101	0.8346	1.4311
0.0418	1.3777	0.4359	1.4158	0.9533	1.4329
0.0999	1.3850	0.5173	1.4211	1.0000	1.4334
0.1188	1.3878	0.5992	1.4245		
Tetraethylene Glycol Dimethyl Ether (1) + Diethyl Carbonate (2)					
0.0000	1.3859	0.4303	1.4138	0.8605	1.4289
0.0420	1.3898	0.5050	1.4169	0.9065	1.4308
0.0801	1.3921	0.5900	1.4198	0.9390	1.4313
0.1353	1.3960	0.6994	1.4241	0.9752	1.4321
0.2034	1.4009	0.7611	1.4262	1.0000	1.4334
0.3367	1.4080	0.8213	1.4275		
Tetraethylene Glycol Dimethyl Ether (1) + Propylene Carbonate (2)					
0.0000	1.4210	0.2818	1.4281	0.7844	1.4315
0.0221	1.4229	0.3885	1.4292	0.8659	1.4322
0.0763	1.4251	0.4955	1.4297	0.9146	1.4330
0.1074	1.4260	0.5506	1.4302	0.9450	1.4332
0.1524	1.4268	0.6567	1.4310	1.0000	1.4334
0.2095	1.4275				

The various values of the coefficients a_k obtained by unweighted least-squares regression are given in Table 3 along with the standard deviation $\sigma(V_m^E)$ defined as

$$\sigma(V_m^E) = [\sum(V_{m,exptl}^E - V_{m,calcd}^E)^2/(n_{obs} - n)]^{0.5} \qquad (2)$$

where n_{obs} is the number of experimental points.

The excess volumes at 298.15 K are plotted against the mole fraction (x_1) of tetraethylene glycol dinethyl ether in Figure 1. We note that V_m^E is negative over the whole range in the three mixtures and decreases in the sequence diethyl carbonate < dimethyl carbonate < propylene carbonate. Similar variations in V_m^E occur in mixtures of diethylene glycol dimethyl ether or triethylene glycol dimethyl ether with esters of carbonic acid (Pal and Kumar, 1998; Pal et al., 1998). The value of V_m^E decreases as the number of diethylene glycol units [CH_2CH_2O] in the polyether chain increases. Thus, the presence of oxygen atom in the polyether chain lowers the excess values for the mixtures containing esters of carbonic acid. The results for negative V_m^E suggest specific but complex pattern for the interaction between molecules. Among several effect and balancing forces, the dipole−dipole interactions within the molecules are dominating in all mixtures. On the other hand, it is important to note which dipole moment of propylene carbonate is fairly high in comparison to that of dimethyl carbonate or diethyl carbonate, resulting in a

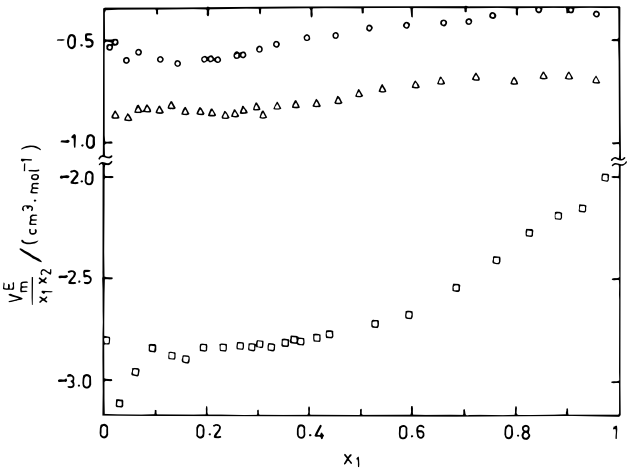

Figure 2. Reduced excess molar volume (V_m^E/x_1x_2), of binary mixtures containing tetraethylene glycol dimethyl ether + dimethyl carbonate (○), + diethyl carbonate (△), and + propylene carbonate (□) at 298.15 K.

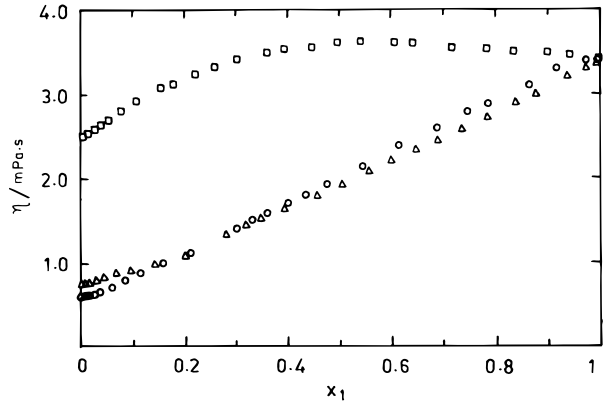

Figure 3. Dynamic viscosity (η) of binary mixtures containing tetraethylene glycol dimethyl ether + dimethyl carbonate (○), + diethyl carbonate (△), and + propylene carbonate (□) at 298.15 K.

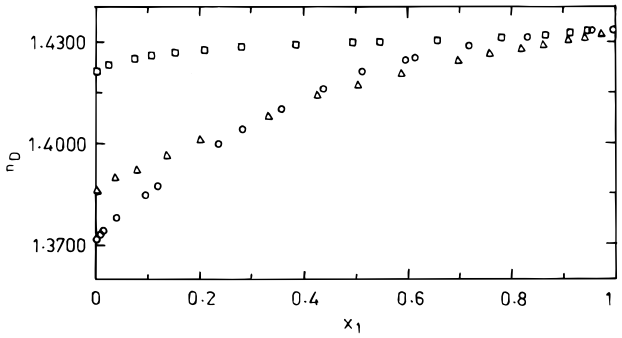

Figure 4. Refractive index (n_D) of binary mixtures containing tetraethylene glycol dimethyl ether + dimethyl carbonate (○), + diethyl carbonate (△), and + propylene carbonate (□) at 298.15 K.

negative contribution to V_m^E with moderately polar solvent, tetraethylene glycol dimethyl ether. Again the behavior is consistent with that of the V_m^E for the polyethers with ethyl acetate (Tovar et al., 1997) or for the dialkyl carbonates with branched ether (Francesconi and Comelli, 1997b). Figure 2 shows the reduced excess molar volumes of binary mixtures containing tetraethylene glycol dimethyl ether + esters of carbonic acid at 298.15 K.

The η and n_D results of the mixtures at 298.15 K are shown in Figures 3 and 4, which follow the sequence PC > DEC > DMC in lower x_1. In higher x_1 the sequence is PC > DMC > DEC. Figures 3 and 4 show that the dynamic viscosity as well as the refractive index of the binary liquid mixtures of dimethyl carbonate and diethyl carbonate with tetraethylene glycol dinethyl ether increases whereas for the mixture with propylene carbonate it increases up to $x_1 < 0.55$ and then decreases.

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Received for review May 1, 1998. Accepted August 4, 1988. The authors are thankful to the Department of Science and Technology (DST), New Delhi, for the financial support (Grant No. SP/ S1/H - 16/94) to carry out this work.

JE9800961