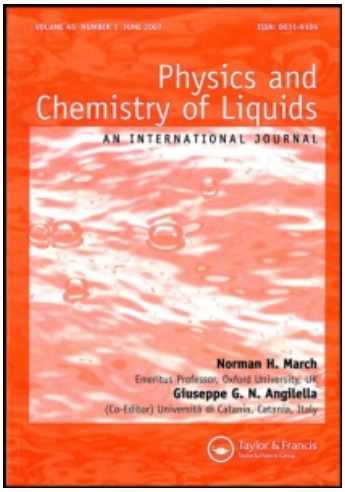

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Excess molar volumes of binary mixtures containing Dipropylene Glycol Monomethyl Ether with Water and 2-Methoxyethanol

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EXCESS MOLAR VOLUMES OF BINARY MIXTURES CONTAINING DIPROPYLENE GLYCOL MONOMETHYL ETHER WITH WATER AND 2-METHOXYETHANOL

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Densities (ρ) at five temperatures, between 293.15 and 313.15 K, of binary mixtures of dipropylene glycol monomethyl ether + water and dipropylene glycol monomethyl ether + 2-methoxyethanol, are reported. The excess molar volumes (V^E) were calculated from these experimental data. The results are discussed in terms of intermolecular interactions.

Keywords: Density; 2-Methoxyethanol; Dipropylene glycol monomethyl ether; Intermolecular interactions

INTRODUCTION

In continuation of our program on the thermodynamic, acoustic, dielectric, and structural properties of some mixtures of alkoxyalcohols with different solvents [1–7] the present article reports density for binary mixtures containing dipropylene glycol monomethyl ether (DPM) with water and 2-methoxyethanol (ME), at various temperatures.

Furthermore, the experimental results are used to disclose the nature of binary interactions in the bulk of the studied binary mixtures.

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EXPERIMENTAL SECTION

Materials

Dipropylene glycol monomethyl ether and 2-methoxyethanol Fluck, pro-analysis, containing less than 0.05% (w/w) of water, respectively (determined by Karl-Fischer method), were used.

Dipropylene glycol monomethyl ether and 2-methoxyethanol, were further purified by the methods described by Pal [9] and Riddick *et al.* [10]. Double distilled, deionized, and degassed water, conductivity better than $1 \times 10^{-7}\ \Omega^{-1}\,\mathrm{cm}^{-1}$, was prepared in our laboratory. The purities of liquids were checked by measuring and comparing the densities at 298.15 K and atmospheric pressure with literature values, as shown in Table I. The mixtures were prepared by mass, with weighing accuracy to $\pm 1 \times 10^{-4}$ g. Conversion to molar quantities was based on the relative atomic mass table of 1985 issued by IUPAC in 1986. The uncertainty in the mole fractions is less than 1×10^{-4}. Liquids were stored in dry-box over phosphoric pentoxide and degassed by ultrasound just before the experiment.

Measurements

Solvent densities were measured with a bicapillary type Lipkin pycnometer, with a capacity of *ca.* 90 cm^3. The pycnometer was calibrated with standard pure liquids, such as propan-1-ol and butan-1-ol. The maximum error in the density measurements was $4 \times 10^{-5}\,\mathrm{g\,cm}^{-3}$.

RESULTS AND DISCUSSION

The experimental data of density (ρ) obtained from the measurements of the pure solvents and for the analyzed binary mixtures at all investigated temperatures are summarized in Table II.

From the measured densities the excess values of molar volumes V^E of the mixtures, at the each investigated temperature, were fitted to the equation:

$$V^E = x_1 \cdot M_1\left(\rho^{-1} - \rho_1^{-1}\right) + x_2 \cdot M_2\left(\rho^{-1} - \rho_2^{-1}\right) \tag{1}$$

where M_1 and M_2 are the molar masses of the pure components and ρ_1, ρ_2, and ρ are the densities of the pure species (1 and 2), and that of the mixtures at different temperatures, respectively.

TABLE I Reference density values of dipropylene glycol monomethyl ether, 2-methoxyethanol, and water, at 298.15 K

Solvent	$\rho/\mathrm{g\,cm}^{-3}$	
	This work	*Lit.*
Dipropylene glycol monomethyl ether	0.95108	0.9527 [8]
2-Methoxyethanol	0.96029	0.960288 [13]
Water	0.99713	0.99707 [10]

TABLE II Experimental density for dipropylene glycol monomethyl ether + water and dipropylene glycol monomethyl ether + 2-methoxyethanol binary mixtures

Dipropylene glycol monomethyl ether + water						*Dipropylene glycol monomethyl ether + 2-methoxyethanol*					
	ρ/g cm^{-3}						ρ/g cm^{-3}				
x_1	*293.15* [K]	*298.15* [K]	*303.15* [K]	*308.15* [K]	*313.15* [K]	x_1	*293.15* [K]	*298.15* [K]	*303.15* [K]	*308.15* [K]	*313.15* [K]
0.0000	0.99828	0.99713	0.99574	0.99411	0.99225	0.0000	0.96488	0.96029	0.95576	0.95110	0.94654
0.0250	1.00659	1.00415	1.00170	0.99896	0.99626	0.0500	0.96426	0.95955	0.95491	0.95016	0.94551
0.0504	1.01036	1.00715	1.00392	1.00052	0.99716	0.1000	0.96369	0.95889	0.95416	0.94934	0.94460
0.0750	1.01136	1.00766	1.00396	1.00015	0.99638	0.1502	0.96317	0.95829	0.95348	0.94859	0.94379
0.1008	1.01067	1.00666	1.00260	0.99850	0.99447	0.2000	0.96268	0.95773	0.95287	0.94792	0.94306
0.1250	1.00908	1.00483	1.00058	0.99632	0.99207	0.2504	0.96221	0.95721	0.95228	0.94728	0.94237
0.1500	1.00684	1.00244	0.99806	0.99367	0.98927	0.3000	0.96176	0.95671	0.95173	0.94668	0.94171
0.1750	1.00426	0.99976	0.99527	0.99078	0.98627	0.3500	0.96132	0.95621	0.95119	0.94610	0.94110
0.1995	1.00159	0.99702	0.99246	0.98789	0.98330	0.4000	0.96087	0.95574	0.95066	0.94554	0.94049
0.3000	0.99104	0.98617	0.98131	0.97645	0.97155	0.4489	0.96045	0.95527	0.95016	0.94501	0.93991
0.3500	0.98654	0.98149	0.97646	0.97145	0.96637	0.5000	0.96001	0.95479	0.94965	0.94446	0.93932
0.3998	0.98264	0.97740	0.97219	0.96698	0.96172	0.5502	0.95959	0.95433	0.94916	0.94394	0.93877
0.4999	0.97637	0.97071	0.96508	0.95946	0.95381	0.6000	0.95918	0.95390	0.94869	0.94344	0.93824
0.5998	0.97163	0.96557	0.95956	0.95357	0.94756	0.6509	0.95877	0.95347	0.94822	0.94295	0.93772
0.6998	0.96766	0.96136	0.95510	0.94886	0.94262	0.7000	0.95841	0.95307	0.94780	0.94250	0.93725
0.7498	0.96580	0.95946	0.95316	0.94688	0.94059	0.7499	0.95804	0.95270	0.94740	0.94208	0.93680
0.8005	0.96394	0.95762	0.95134	0.94509	0.93883	0.7990	0.95771	0.95234	0.94702	0.94169	0.93640
0.8499	0.96212	0.95589	0.94971	0.94355	0.93739	0.8498	0.95739	0.95200	0.94665	0.94131	0.93600
0.8997	0.96027	0.95422	0.94821	0.94223	0.93625	0.9000	0.95709	0.95168	0.94632	0.94096	0.93565
0.9525	0.95831	0.95254	0.94682	0.94112	0.93542	0.9500	0.95680	0.95138	0.94600	0.94064	0.93531
1.0000	0.95651	0.95108	0.94570	0.94034	0.93500	1.0000	0.95651	0.95108	0.94570	0.94034	0.93500

Excess volume was fitted by a Redlich–Kister type equation [11].

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

The parameters a_j of Eq. (2) were evaluated by the least-squares method. The values of these parameters, at each studied temperature, with standard deviation $\rho(V^E)$ are summarized in Table III.

The variations of V^E *versus* the mole fraction of DMP at 298.15 K are presented in Fig. 1, respectively. Figure 1 shows that the excess molar volumes are negative for all the investigated systems, with a minimum positioned always nearly $x_{\text{DPM}} \approx 0.30$ for DPM + H_2O, and nearly $x_{\text{DPM}} \approx 0.45$ for DPM + ME binary mixtures.

The magnitude of the volume concentration follows the sequence:

$$\left|V^E_{\text{DPM}+H_2O}\right| > \left|V^E_{\text{DPM}+\text{ME}}\right|$$

Moreover, the excess volumes were found to increase with the increasing temperature (see Tables II and III). The volumes concentrations are possibly influenced by two effects. The negative values of V^E over the all mole fraction may be attributed mainly to the association through intermolecular hydrogen bonds between DPM and water or ME. Another effect, which would give a negative contribution to the excess

TABLE III Parameters a_j of Eq. (2), and standard deviations $\sigma(V^E)$ for dipropylene glycol monomethyl ether + water and dipropylene glycol monomethyl ether + 2-methoxyethanol binary mixtures

	a_0	a_1	a_2	a_3	a_4	$\sigma(V^E)$
Dipropylene glycol monomethyl ether + water						
T/K			293.15			
V^E/cm^3 mol^{-1}	−5.4946	2.2834	−4.3887	2.4802	−0.1423	0.0011
T/K			298.15			
V^E/cm^3 mol^{-1}	−5.3170	2.9728	−3.7488	2.2553	−0.0840	0.0008
T/K			303.15			
V^E/cm^3 mol^{-1}	−5.1450	3.6713	−3.0426	2.0774	−0.1316	0.0009
T/K			308.15			
V^E/cm^3 mol^{-1}	−4.9729	4.3969	−2.3800	1.8891	−0.1128	0.0010
T/K			313.15			
V^E/cm^3 mol^{-1}	−4.7801	5.1201	−1.6786	1.8171	−0.1832	0.0009
Dipropylene glycol monomethyl ether + 2-methoxyethanol						
T/K			293.15			
V^E/cm^3 mol^{-1}	−0.3303	0.1434	0.1643	−0.1384	−0.1037	0.0005
T/K			298.15			
V^E/cm^3 mol^{-1}	−0.2992	0.1383	0.1637	−0.1551	−0.0640	0.0005
T/K			303.15			
V^E/cm^3 mol^{-1}	−0.2782	0.1357	0.1896	−0.1446	−0.0421	0.0004
T/K			308.15			
V^E/cm^3 mol^{-1}	−0.2497	0.1462	0.2294	−0.1426	−0.0651	0.0005
T/K			313.15			
V^E/cm^3 mol^{-1}	−0.2243	0.1711	0.2403	−0.1826	−0.0656	0.0006

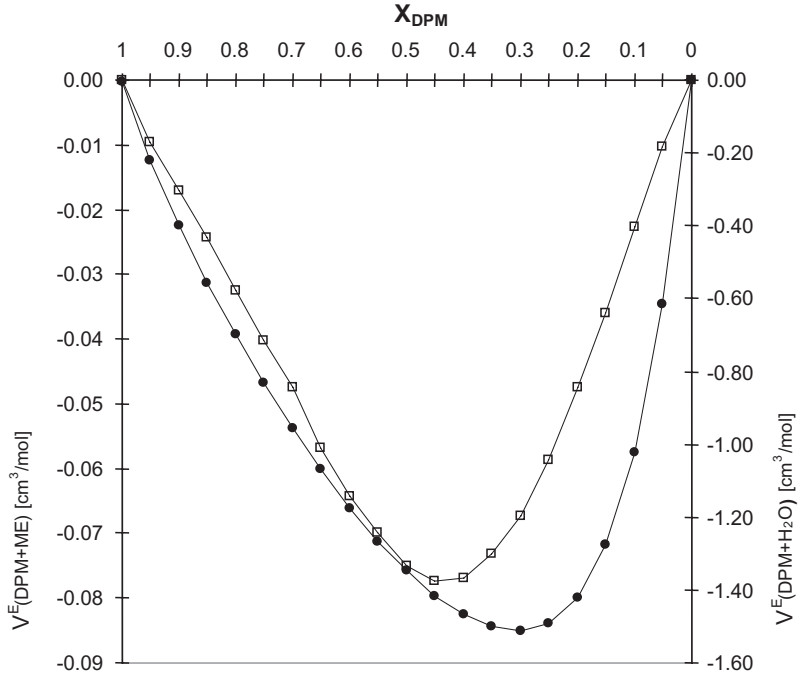

FIGURE 1 Plot of V^E as a function of composition for DPM + H_2O (●) and DPM + ME (□), at 298.15 K.

volumes, is the difference in molecular sizes between the two components in the binary mixtures (this is a geometrical effect). As these differences increase, the more negative would be the contribution to V^E [8,12–15].

In the mixtures studied the DPM, ME, and water molecules have different molar volumes as pure species:

$$V(H_2O) = 18.068\,cm^3\,mol^{-1} < V(ME) = 79.242\,cm^3\,mol^{-1} < V(DPM) = 155.828\,cm^3\,mol^{-1}$$

therefore this effect should be significant and of great importance. The difference in the free volumes between dipropylene glycol monomethyl ether, 2-methoxyethanol, and water would facilitate the penetration of one component (water or ME) into the others (DPM).

After these considerations, we may assume that in the DPM + ME and DPM + H_2O liquid mixtures all the effects discussed above should be taken into account and may contribute to V^E values.

The results obtained in this work seem to indicate that the respective stable intermolecular complexes of the DPM · $2H_2O$ or DPM · ME types would be formed in the studied binary mixtures of dipropylene glycol monomethyl ether + water or dipropylene glycol monomethyl ether + 2-methoxyethanol.

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