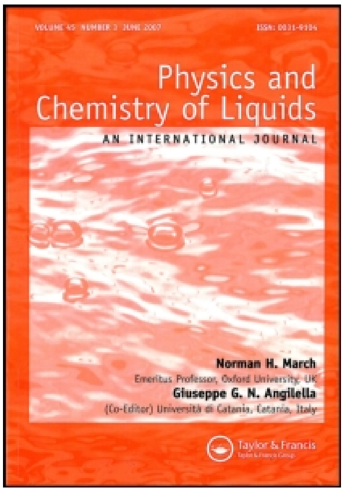

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Dielectric properties of binary mixtures of dipropylene glycol monomethyl ether with 2-methoxyethanol and water at various temperatures

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Dielectric properties of binary mixtures of dipropylene glycol monomethyl ether with 2-methoxyethanol and water at various temperatures

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Relative permittivities (ε) 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 in this article. The relative permittivity deviations ($\Delta\varepsilon$) were calculated from these experimental data. The results are discussed in terms of intermolecular interactions.

Keywords: Dipropylene glycol monomethyl ether; 2-Methoxyethanol; Relative permittivity; Binary liquid mixtures

1. Introduction

In continuation of our program on the thermodynamic, acoustic, dielectric and transport properties of some mixtures of alkoxyalcohols with different solvents [1–7], the present article reports relative permittivities for binary mixtures containing dipropylene glycol monomethyl ether (DPM) with water and 2-methoxyethanol (ME) at various temperatures. We calculated the deviations of the relative permittivity, which were fitted to the Redlich–Kister equation [8]. 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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2. Experimental

2.1 *Materials*

Dipropylene glycol monomethyl ether (DPM) and 2-methoxyethanol (ME) Merck, pro-analysis, containing less than 0.05% (w/w) of water (determined by Karl-Fischer method), were used. The purities of these compounds were checked by comparing the measured densities with those reported in the literature and also by the chromatographic method. No further purification was considered necessary, but the dipropylene glycol monomethyl ether and 2-methoxyethanol were dried with molecular sieves, Type 0.3 nm from Merck. These solvents were stored in a dry-box over phosphoric pentoxide. Double-distilled, deionized, and degassed water, of conductivity better than $10^{-7}\,\Omega^{-1}\,\mathrm{cm}^{-1}$, was prepared in our laboratory.

All solvents were degassed by ultrasound just before the experiment. The measured densities of the pure compounds at 298.15 K, along with literature values, are given in table 1.

2.2 *Measurements*

The relative permittivity measurements were carried out at 3 MHz, using a bridge of the type OH-301 (made in Radelcis, Hungary). The thermostatted stainless steel measuring cells were of C3 ($1 < \varepsilon < 25$) and C4 ($25 < \varepsilon < 90$) type. The cells were calibrated with standard pure liquids, such as acetone, butan-1-ol, dichloromethane, and deionized water. All the organic solvents were of spectrograde quality or higher. The relative permittivities for the standards were taken from the literature [9]. The uncertainty in the relative permittivity measurements was ± 0.02.

In all the dielectric property measurements, a Haake Model DC-30 thermostat was used with a constant digital temperature control of ± 0.01 K. The mixtures were prepared using a Sartorius balance. The maximum estimated error in the mole fractions is $\pm 10^{-4}$.

3. Results and discussion

The experimental data for the relative permittivity (ε) obtained from the measurements of the pure solvents and for the analyzed binary mixtures at all investigated temperatures are reported in table 2. Many investigations of the dielectric behaviour

Table I. Reference density and relative permittivity values of dipropylene glycol monomethyl ether, 2-methoxyethanol, and water at 298.15 K.

	ρ ($\mathrm{g \cdot cm^{-3}}$)		ε	
Solvent	This work	Literature	This work	Literature
Dipropylene glycol monomethyl ether	0.95108	0.9527 [14]	10.40	_
2-Methoxyethanol	0.96029	0.960288 [15]	16.96	16.94 [12]
Water	0.99713	0.99707 [16]	78.48	78.64 [16]

Table 2. Experimental relative permittivity for dipropylene glycol monomethyl ether (DPM) + water and dipropylene glycol monomethyl ether + 2-methoxyethanol (ME) binary mixtures.

	DPM + H_2O						DPM + ME				
	293.15 (K)	298.15 (K)	303.15 (K)	308.15 (K)	313.15 (K)		293.15 (K)	298.15 (K)	303.15 (K)	308.15 (K)	313.15 (K)
x_1			ε			x_1			ε		
0.0000	80.38	78.48	76.72	74.97	73.12	0.0000	17.41	16.96	16.59	16.16	15.78
0.0250	71.12	69.44	67.90	66.39	64.99	0.0500	16.74	16.37	16.04	15.65	15.32
0.0504	62.98	61.48	60.09	58.77	57.67	0.1000	16.15	15.79	15.49	15.12	14.80
0.0750	56.23	54.86	53.62	52.43	51.50	0.1502	15.61	15.28	14.98	14.60	14.28
0.1008	50.20	48.95	47.80	46.72	45.91	0.2000	15.15	14.78	14.48	14.10	13.77
0.1250	45.39	44.22	43.15	42.14	41.38	0.2504	14.69	14.32	14.02	13.64	13.30
0.1500	41.16	40.07	39.05	38.10	37.36	0.3000	14.30	13.91	13.60	13.22	12.89
0.1750	37.57	36.54	35.58	34.66	33.91	0.3500	13.90	13.52	13.20	12.83	12.50
0.1995	34.58	33.61	32.68	31.80	31.05	0.4000	13.54	13.16	12.84	12.47	12.14
0.3000	26.32	25.50	24.70	23.93	23.15	0.4489	13.19	12.83	12.52	12.15	11.83
0.3500	23.75	22.98	22.24	21.53	20.80	0.5000	12.88	12.52	12.21	11.84	11.53
0.3998	21.77	21.05	20.36	19.70	19.05	0.5502	12.56	12.23	11.92	11.56	11.25
0.4999	18.70	18.07	17.50	16.96	16.46	0.6000	12.30	11.96	11.67	11.30	11.00
0.5998	16.24	15.69	15.21	14.76	14.36	0.6509	12.03	11.71	11.41	11.07	10.77
0.6998	14.21	13.72	13.31	12.91	12.51	0.7000	11.81	11.47	11.18	10.84	10.56
0.7498	13.38	12.91	12.54	12.15	11.75	0.7499	11.58	11.25	10.98	10.65	10.35
0.8005	12.67	12.24	11.89	11.53	11.12	0.7990	11.37	11.05	10.78	10.46	10.17
0.8499	12.10	11.71	11.38	11.04	10.66	0.8498	11.18	10.84	10.59	10.28	10.00
0.8997	11.63	11.26	10.94	10.63	10.30	0.9000	11.02	10.69	10.42	10.12	9.85
0.9525	11.17	10.81	10.50	10.19	9.90	0.9500	10.85	10.54	10.27	9.95	9.67
1.0000	10.76	10.40	10.12	9.77	9.49	1.0000	10.76	10.40	10.12	9.77	9.49

of liquids have been reported in the literature and the best representation of the results as a function of temperature is given by the following equation [10]:

$$\ln \varepsilon = \alpha_0 + \alpha T \tag{1}$$

where α_i $(i = 0, 1)$ are empirical constants and T is the absolute temperature. The α_i coefficients of this fitting procedure are listed in table 3, along with the standard deviations σ $(\ln \varepsilon)$ for each binary mixture.

Equation (1) reproduces the experimental relative permittivity values with an average uncertainty, evaluated by means of the relation:

$$\overline{\Delta\varepsilon} = \frac{\sum \left|\varepsilon_{\text{cal}} - \varepsilon_{\text{exp}}\right|}{N} \tag{2}$$

where N is the number of experimental points. The values of $\overline{\Delta\varepsilon} = \pm 0.02$ units for DPM + ME and DPM + H_2O binary liquid mixtures.

The variation of relative permittivity with composition was studied by using the following equation:

$$\ln \varepsilon = \sum_{j=0}^{4} \beta_j x_1^j \tag{3}$$

Table 3. Coefficients α_i and standard deviations $\sigma(\ln\varepsilon)$ of e.g. (1) for DPM + H_2O and DPM + ME binary mixtures.

DPM + H_2O				DPM + ME			
x_1	α_0	α_1	$10^3\cdot\sigma(\ln\varepsilon)$	x_1	α_0	α_1	$10^3\cdot\sigma(\ln\varepsilon)$
0.0000	5.765099	−0.004702	0.7	0.0000	4.292560	−0.004898	1.1
0.0250	5.583838	−0.004504	0.8	0.0500	4.121170	−0.004445	1.0
0.0504	5.438530	−0.004425	1.8	0.1000	4.059823	−0.004359	1.2
0.0750	5.323626	−0.004421	2.2	0.1502	4.060060	−0.004473	1.7
0.1008	5.234879	−0.004506	2.6	0.2000	4.114243	−0.004762	1.5
0.1250	5.180287	−0.004663	2.7	0.2504	4.138344	−0.004949	1.6
0.1500	5.147009	−0.004883	2.5	0.3000	4.175465	−0.005170	1.4
0.1750	5.136259	−0.005156	2.0	0.3500	4.183660	−0.005294	1.1
0.1995	5.129304	−0.005414	1.6	0.4000	4.202037	−0.005443	1.1
0.3000	5.148046	−0.006404	0.5	0.4489	4.175036	−0.005442	1.3
0.3500	5.105134	−0.006609	0.6	0.5000	4.181551	−0.005546	1.4
0.3998	5.034012	−0.006664	2.0	0.5502	4.153372	−0.005533	1.4
0.4999	4.794881	−0.006372	1.5	0.6000	4.152866	−0.005603	1.9
0.5998	4.586101	−0.006143	2.3	0.6509	4.115044	−0.005550	1.2
0.6998	4.503184	−0.006314	1.5	0.7000	4.111712	−0.005605	1.3
0.7498	4.471497	−0.006410	1.7	0.7499	4.087621	−0.005588	1.6
0.8005	4.419317	−0.006415	2.2	0.7990	4.060796	−0.005559	1.4
0.8499	4.324376	−0.006247	1.9	0.8498	4.032162	−0.005523	1.8
0.8997	4.214336	−0.006009	1.2	0.9000	4.036195	−0.005586	1.2
0.9525	4.473484	−0.006009	1.2	0.9500	4.072442	−0.005758	1.4
1.0000	4.214225	−0.006272	1.4	1.0000	4.214225	−0.006272	1.4

Table 4. Coefficients β_j and standard deviations $\sigma(\ln\varepsilon)$ of e.g. (3) for DPM + H_2O and DPM + ME binary mixtures, at various temperatures.

T (K)	β_0	β_1	β_2	β_3	β_4	$10^3\cdot\sigma(\ln\varepsilon)$
DPM + H_2O						
293.15	4.400605	−5.672274	8.496592	−7.518041	2.671248	7.9
298.15	4.377039	−5.683283	8.393681	−7.305447	2.562639	8.3
303.15	4.355455	−5.706618	8.316856	−7.086165	2.436367	8.8
308.15	4.333422	−5.709571	8.143326	−6.708047	2.222506	9.8
313.15	4.312730	−5.685954	7.882059	−6.285341	2.027720	13.0
DPM + ME						
293.15	2.856269	−0.786790	0.547436	−0.464640	0.222800	0.9
298.15	2.831762	−0.759628	0.364797	−0.160001	0.064585	0.8
303.15	2.809952	−0.718819	0.126028	0.219607	−0.122860	0.8
308.15	2.783886	−0.687214	−0.097610	0.599677	−0.319255	0.8
313.15	2.761285	−0.675747	−0.209847	0.789535	−0.415067	1.4

which could be fitted to the experimental data at each temperature using a least-squares method [10]. The values of β_j coefficients and the standard deviations $\sigma(\ln\varepsilon)$ are reported in table 4. The goodness-of-fit of this procedure is ascertained by a mean deviation $\overline{\Delta\varepsilon} = \pm 0.02$ units for DPM + DPM and $\overline{\Delta\varepsilon} = \pm 0.04$ units for ME + H_2O binary mixtures.

The difference between the real dielectric behaviour of DPM + ME and DPM + H_2O binary mixtures and ideal behaviour, according to Payne and Theodorou [11], has been evaluated by means of the equation:

$$\Delta\varepsilon = \varepsilon - (\varepsilon_1 x_1 + \varepsilon_2 x_2) \qquad (4)$$

Table 5. Deviations of the relative permittivity for dipropylene glycol monomethyl ether + water and dipropylene glycol monomethyl ether + 2-methoxyethanol binary mixtures.

	DPM + H_2O						DPM + ME				
	293.15 (K)	298.15 (K)	303.15 (K)	308.15 (K)	313.15 (K)		293.15 (K)	298.15 (K)	303.15 (K)	308.15 (K)	313.15 (K)
x_1	$\Delta\varepsilon$					x_1	$\Delta\varepsilon$				
0.0000	0.00	0.00	0.00	0.00	0.00	0.0000	0.00	0.00	0.00	0.00	0.00
0.0250	−7.52	−7.34	−7.16	−6.95	−6.54	0.0500	−0.34	−0.26	−0.23	−0.19	−0.15
0.0504	−13.89	−13.57	−13.27	−12.91	−12.24	0.1000	−0.60	−0.52	−0.45	−0.40	−0.35
0.0750	−18.93	−18.51	−18.11	−17.65	−16.85	0.1502	−0.80	−0.70	−0.64	−0.60	−0.56
0.1008	−23.16	−22.67	−22.21	−21.68	−20.80	0.2000	−0.93	−0.87	−0.82	−0.78	−0.75
0.1250	−26.29	−25.75	−25.25	−24.68	−23.79	0.2504	−1.05	−1.00	−0.95	−0.92	−0.90
0.1500	−28.78	−28.20	−27.68	−27.09	−26.22	0.3000	−1.12	−1.09	−1.05	−1.03	−1.00
0.1750	−30.63	−30.03	−29.49	−28.90	−28.07	0.3500	−1.18	−1.15	−1.13	−1.10	−1.08
0.1995	−31.91	−31.29	−30.75	−30.16	−29.38	0.4000	−1.21	−1.18	−1.16	−1.14	−1.12
0.3000	−33.17	−32.56	−32.04	−31.48	−30.88	0.4489	−1.23	−1.19	−1.17	−1.15	−1.13
0.3500	−32.26	−31.67	−31.17	−30.62	−30.05	0.5000	−1.21	−1.17	−1.15	−1.13	−1.11
0.3998	−30.78	−30.21	−29.73	−29.20	−28.63	0.5502	−1.19	−1.13	−1.11	−1.09	−1.07
0.4999	−26.88	−26.38	−25.93	−25.42	−24.85	0.6000	−1.12	−1.07	−1.04	−1.03	−1.01
0.5998	−22.38	−21.96	−21.56	−21.10	−20.59	0.6509	−1.05	−0.99	−0.97	−0.94	−0.92
0.6998	−17.45	−17.12	−16.80	−16.43	−16.08	0.7000	−0.95	−0.91	−0.88	−0.85	−0.82
0.7498	−14.80	−14.52	−14.24	−13.93	−13.66	0.7499	−0.84	−0.80	−0.76	−0.73	−0.71
0.8005	−11.98	−11.74	−11.52	−11.25	−11.06	0.7990	−0.73	−0.68	−0.64	−0.60	−0.58
0.8499	−9.11	−8.91	−8.74	−8.52	−8.38	0.8498	−0.58	−0.55	−0.50	−0.46	−0.43
0.8997	−6.11	−5.97	−5.86	−5.68	−5.57	0.9000	−0.41	−0.38	−0.35	−0.30	−0.27
0.9525	−2.90	−2.82	−2.78	−2.68	−2.61	0.9500	−0.24	−0.20	−0.17	−0.15	−0.13
1.0000	0.00	0.00	0.00	0.00	0.00	1.0000	0.00	0.00	0.00	0.00	0.00

where: ε_1, ε_2 and ε are the relative permittivities of the DPM, ME or H_2O, and the mixtures, respectively. The values of $\Delta\varepsilon$ for the investigated systems are listed in table 5.

The variations of $\Delta\varepsilon$ with the mole fraction of dipropylene glycol monomethyl ether (x_1) at 298.15 K are presented in figure 1. The curves have been obtained by fitting the $\Delta\varepsilon$ with a Redlich–Kister equation of the type [8]:

$$\Delta\varepsilon = x_1(1 - x_1)\sum_{j=0}^{4} a_j(2x_1 - 1)^j \tag{5}$$

Figure 1 shows that the relative permittivity deviations are always negative for each binary system, and that they become less negative when temperature increases (see table 5), with a minimum lying always nearly $x_{\mathrm{DPM}} \approx 0.30$ for DPM + H_2O, and nearly $x_{\mathrm{DPM}} \approx 0.45$ for DPM + ME binary mixtures.

As suggested by other authors [11–13], the study of this extra-thermodynamic parameter for binary liquid systems represents a unique tool for investigating the formation of intermolecular complexes, and provides a valuable aid for determining their stoichiometry and relative stability. The position of the relative minima in the plots of $\Delta\varepsilon$ *versus* x_1 could be taken as the true composition of these intermolecular complexes.

The results obtained in this work seem to indicate that the molecules of studied binary mixtures may be joined, by a network of interactions such as dipolar and

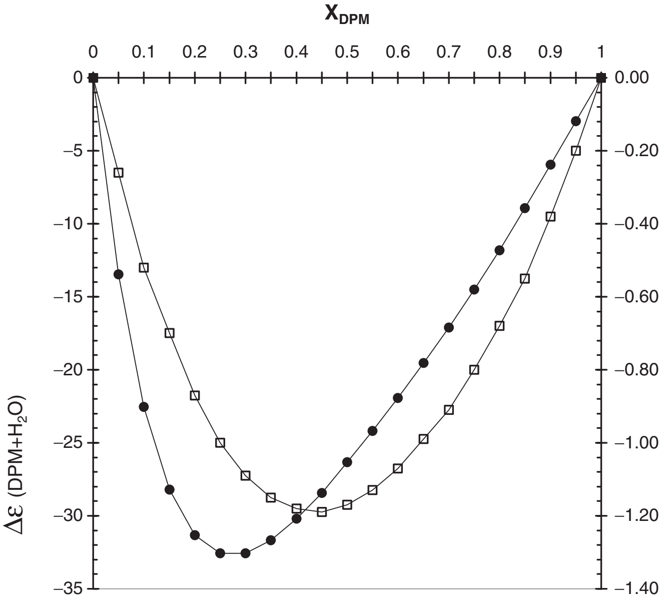

Figure 1. Plot of $\Delta\varepsilon$ as a function of composition for DPM + H_2O (●) and DPM + ME (☐), at 298.15 K.

hydrogen bonds, to form stable intermolecular complexes of the DPM·2H_2O or DPM·ME types.

On the basis of comparison of $\Delta\varepsilon$ values in the composition regions corresponding to their maximum deviation from ideality (see table 5), it is possible to deduce that:

$$|\Delta\varepsilon_{\mathrm{DPM+H_2O}}| \gg |\Delta\varepsilon_{\mathrm{DPM+ME}}|$$

Therefore, it is necessary to assume that the energetic stability of intermolecular complexes DPM·2H_2O and DPM·ME changes in an identical way.

Similar conclusions were derived in our previous paper, where we investigated the volumetric properties for binary mixtures containing dipropylene glycol monomethyl ether (DPM) with water and 2-methoxyethanol (ME), at various temperatures [7]. The excess molar volumes were negative for all the investigated systems, with a minimum lying always near $x_{\mathrm{DPM}} \approx 0.30$ for DPM + H_2O, and near $x_{\mathrm{DPM}} \approx 0.45$ for DPM + ME binary mixtures.

The magnitude of the volume concentration followed a similar relationship as $\Delta\varepsilon$:

$$\left|V^{\mathrm{E}}_{\mathrm{DPM+H_2O}}\right| > \left|V^{\mathrm{E}}_{\mathrm{DPM+ME}}\right|$$

The negative values of V^{E} have been explained by considering the chemical or specific interactions, which may result from differences in molecular volumes and free volumes, possible association by hydrogen bonds between unlike molecules and dipole–dipole interactions.

The results of $\Delta\varepsilon$ presented in this article support these suggestions.

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