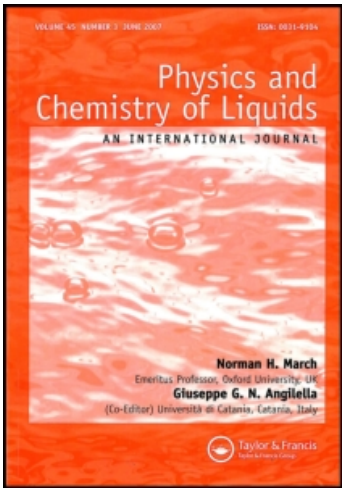

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Refractive properties of binary mixtures containing 2-methoxyethanol and diethylamine, triethylamine, and propylamine

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REFRACTIVE PROPERTIES OF BINARY MIXTURES CONTAINING 2-METHOXYETHANOL AND DIETHYLAMINE, TRIETHYLAMINE, AND PROPYLAMINE

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Refractive indexes (n_D) of numerous binary mixtures of 2-methoxyethanol + diethylamine, 2-methoxyethanol + triethylamine, and 2-methoxyethanol + propylamine, between 288.15 and 308.15 K, are reported. Furthermore, the excess molar refraction (R^E) and deviation from ideality refractive index (Δn_D) have been examined, in order to identify the presence of intermolecular complexes in these binary liquid mixtures.

Keywords: Refractive index; 2-Methoxyethanol; Diethylamine; Triethylamine; Propylamine; Binary liquid mixtures

1. INTRODUCTION

The knowledge of the physicochemical and thermodynamic properties of binary liquid mixtures formed by one or two components associated through hydrogen bonds is important from both theoretical and process design aspects. Excess thermodynamic properties, which depend on the composition or/and temperature, are of great importance in helping to understand the nature of molecular aggregation that exists in the binary mixtures [1–3].

In continuation of our program on the structural properties of some mixtures of 2-methoxyethanol with aliphatic amines [4–9], the present article reports the refractive index for 2-methoxyethanol + diethylamine, 2-methoxyethanol + triethylamine, and 2-methoxyethanol + propylamine, at various temperatures.

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

2. EXPERIMENTAL

2.1. Materials

2-methoxyethanol, diethylamine, triethylamine, and propylamine Merck, pro-analysis, containing less than 0.05% (w/w) of water, respectively (determined by Karl-Fischer method), were used. 2-Methoxyethanol and aliphatic amines were further purified by the methods reported by Riddick *et al.* [10]. The mixtures were prepared by weighing with an accuracy of $\pm 1 \times 10^{-4}$ g. The conversions to molar quantities were based on the relative atomic mass table (1985), issued by IUPAC in 1986. The uncertainty in the mole fractions is less than 1×10^{-4}. All liquids were stored in a dry-box over P_2O_5, and were degassed by ultrasounds just before the experiments. Experimental data of refractive indexes for the pure solvents, at 298.15 K, are compared with values available in the literature and listed in Table I. The differences between the measured and literature values can be ascribed to the differing measurement method used, and to the different sample purification procedures employed by the authors [11].

2.2. Measurements

The refractive indexes n_D (Na–D line, at $\lambda = 589$ nm) were measured by an automatic refractometer DR 5000 Krüss, with a resolution of 1×10^{-5} and an accuracy of 3×10^{-5}. In all the refractive properties measurements, an Haake model DC-30 thermostat was used at a constant digital temperature control of ± 0.01 K.

3. RESULTS AND DISCUSION

The experimental data of the refractive index (n_D) obtained from the measurements of the pure solvents and for the analyzed binary mixtures at all investigated temperatures are summarized in Tables II–IV.

Many authors have been recommended for the refractometric analysis of intermolecular interactions in liquid binary mixtures to study deviations from additivity of the coefficient n_D plotted as a function of the concentration expressed as a mole fraction [12–14]. However, this method has a certain theoretical foundation only for liquid

TABLE I Reference refractive index values of 2-methoxyethanol, diethylamine, triethylamine, and propylamine, at 298.15 K

Solvent	n_D	
	This work	*Lit.*
2-Methoxyethanol	1.40057	1.4007 [20] 1.40046 [21]
Diethylamine	1.38168	1.38170 [22]
Triethylamine	1.39825	1.3980 [23,24]
Propylamine	1.38503	1.3851 [24,25]

TABLE II Experimental refractive index (ρ) and deviations refractive index (V^E) for 2-methoxyethanol (**1**) + diethylamine (**2**) binary mixtures

x_1	ϕ_1	n_D				Δn_D			
		291.15 K	*293.15* K	*298.15* K	*303.15* K	*291.15* K	*293.15* K	*298.15* K	*303.15* K
0.0000	0.0000	1.38591	1.38470	1.38168	1.37865	0.00000	0.00000	0.00000	0.00000
0.0500	0.0700	1.38790	1.38665	1.38362	1.38046	0.00114	0.00108	0.00101	0.00083
0.1000	0.1370	1.38990	1.38862	1.38560	1.38244	0.00228	0.00218	0.00207	0.00182
0.1499	0.2013	1.39162	1.39029	1.38733	1.38425	0.00315	0.00298	0.00287	0.00265
0.2001	0.2634	1.39332	1.39206	1.38917	1.38614	0.00400	0.00388	0.00378	0.00356
0.2500	0.3227	1.39493	1.39366	1.39086	1.38792	0.00476	0.00461	0.00455	0.00435
0.3000	0.3799	1.39652	1.39529	1.39249	1.38956	0.00549	0.00537	0.00525	0.00501
0.3498	0.4347	1.39792	1.39668	1.39395	1.39106	0.00605	0.00589	0.00579	0.00553
0.4000	0.4879	1.39923	1.39804	1.39533	1.39246	0.00650	0.00638	0.00624	0.00595
0.4498	0.5388	1.40037	1.39917	1.39652	1.39371	0.00679	0.00664	0.00651	0.00622
0.4995	0.5879	1.40135	1.40019	1.39760	1.39483	0.00692	0.00679	0.00666	0.00636
0.5500	0.6359	1.40218	1.40104	1.39850	1.39580	0.00689	0.00676	0.00663	0.00634
0.5999	0.6818	1.40282	1.40168	1.39918	1.39660	0.00668	0.00654	0.00638	0.00616
0.6495	0.7259	1.40326	1.40213	1.39972	1.39724	0.00628	0.00612	0.00600	0.00582
0.7000	0.7693	1.40351	1.40244	1.40008	1.39768	0.00566	0.00555	0.00543	0.00527
0.7500	0.8109	1.40362	1.40256	1.40027	1.39798	0.00492	0.00480	0.00469	0.00458
0.8000	0.8511	1.40359	1.40254	1.40030	1.39804	0.00404	0.00391	0.00380	0.00366
0.8501	0.8902	1.40344	1.40244	1.40025	1.39801	0.00304	0.00294	0.00282	0.00265
0.8998	0.9279	1.40327	1.40231	1.40018	1.39799	0.00202	0.00194	0.00183	0.00165
0.9500	0.9645	1.40303	1.40210	1.40005	1.39795	0.00092	0.00086	0.00077	0.00062
1.0000	1.0000	1.40296	1.40211	1.40021	1.39831	0.00000	0.00000	0.00000	0.00000

system composed from nonpolar or weakly polar and not associated components. Fialkov and Fenerly stated that the refractive index is an additive property of the pure polar and associated components when the composition is expressed in volume fraction (ϕ_i) [15,16].

Following the suggestions of these authors, we have calculated the deviations Δn_D of the experimental values of the mixtures from corresponding values calculated by using the volume fraction mixture law:

$$\Delta n_D = n_D - (\phi_1 \cdot n_1 + \phi_1 \cdot n_2) \tag{1}$$

The values of Δn_D of the studied binary mixtures, at all measured temperatures, are given in Tables II–IV.

For reasons of clarity, only the variations of Δn_D values *versus* the volume fraction of 2-methoxyethanol (ϕ_1) at one temperature ($T = 298.15$ K) for all the studied mixtures are represented in the Fig. 1. The curves have been obtained by fitting the Δn_D with a Redlich–Kister equation of the type [17]:

$$\Delta n_D = \phi_1 \cdot (1 - \phi_1) \sum_{j=0}^{4} a_j \cdot (2\phi_1 - 1)^j \tag{2}$$

In the present binary mixtures, the refractive index deviations are positive for each binary mixtures, with a maximum lying always nearly at $\phi_1 \approx 0.60$ for ME with diethylamine and propylamine, and $\phi_1 \approx 0.55$ for ME with triethylamine (corresponding to $x_1 \approx 0.50$ for ME with DEA and PA, and $x_1 \approx 0.55$ for ME with TEA) binary mixtures.

TABLE III Experimental refractive index (n_D) and deviations refractive index (Δn_D) for 2-methoxyethanol (**1**) + triethylamine (**2**) binary mixtures

x_1	ϕ_1	n_D				
		293.15 K	*298.15* K	*303.15* K	*308.15* K	*313.15* K
0.0000	0.0000	1.40040	1.39825	1.39555	1.39230	1.38850
0.0500	0.0504	1.40118	1.39892	1.39618	1.39289	1.38910
0.1020	0.1028	1.40192	1.39966	1.39694	1.39367	1.38997
0.1502	0.1514	1.40260	1.40035	1.39765	1.39444	1.39081
0.2001	0.2017	1.40328	1.40106	1.39839	1.39525	1.39178
0.3011	0.3037	1.40452	1.40233	1.39973	1.39674	1.39353
0.3501	0.3532	1.40509	1.40288	1.40035	1.39743	1.39432
0.4005	0.4041	1.40556	1.40334	1.40086	1.39803	1.39504
0.4508	0.4549	1.40621	1.40378	1.40133	1.39857	1.39567
0.5002	0.5049	1.40638	1.40406	1.40168	1.39898	1.39621
0.5503	0.5555	1.40645	1.40426	1.40191	1.39927	1.39662
0.5998	0.6056	1.40643	1.40435	1.40204	1.39946	1.39695
0.6499	0.6563	1.40631	1.40433	1.40206	1.39957	1.39719
0.6995	0.7066	1.40609	1.40423	1.40200	1.39956	1.39731
0.7498	0.7575	1.40609	1.40403	1.40184	1.39949	1.39734
0.7992	0.8076	1.40580	1.40371	1.40155	1.39926	1.39721
0.8504	0.8595	1.40533	1.40329	1.40115	1.39893	1.39699
0.8998	0.9090	1.40465	1.40260	1.40051	1.39835	1.39653
0.9499	0.9615	1.40363	1.40162	1.39960	1.39753	1.39586
1.0000	1.0000	1.40211	1.40021	1.39831	1.39642	1.39499
				Δn_D		
0.0000	0.0000	0.00000	0.00000	0.00000	0.00000	0.00000
0.0500	0.0504	0.00069	0.00057	0.00049	0.00038	0.00028
0.1020	0.1028	0.00135	0.00121	0.00111	0.00095	0.00081
0.1502	0.1514	0.00194	0.00181	0.00169	0.00152	0.00134
0.2001	0.2017	0.00254	0.00242	0.00229	0.00213	0.00198
0.3011	0.3037	0.00361	0.00349	0.00335	0.00320	0.00308
0.3501	0.3532	0.00409	0.00394	0.00383	0.00369	0.00355
0.4005	0.4041	0.00448	0.00431	0.00420	0.00408	0.00394
0.4508	0.4549	0.00475	0.00465	0.00454	0.00441	0.00424
0.5002	0.5049	0.00495	0.00483	0.00475	0.00462	0.00446
0.5503	0.5555	0.00504	0.00493	0.00484	0.00470	0.00455
0.5998	0.6056	0.00502	0.00492	0.00483	0.00469	0.00456
0.6499	0.6563	0.00492	0.00481	0.00472	0.00459	0.00447
0.6995	0.7066	0.00471	0.00461	0.00452	0.00438	0.00427
0.7498	0.7575	0.00441	0.00431	0.00422	0.00410	0.00397
0.7992	0.8076	0.00403	0.00389	0.00379	0.00367	0.00352
0.8504	0.8595	0.00348	0.00337	0.00325	0.00313	0.00297
0.8998	0.9090	0.00271	0.00259	0.00248	0.00234	0.00219
0.9499	0.9615	0.00161	0.00151	0.00143	0.00132	0.00120
1.0000	1.0000	0.00000	0.00000	0.00000	0.00000	0.00000

As evidenced from the calculations, the refractive index deviations decrease with an increase of the temperature (see Tables II–IV).

It is known that graphs analogous to that shown in Fig. 1 can be applied to confirm the presence of stable intermolecular complexes in binary liquid mixtures, whose stoichiometric composition can be fixed on the abscissa in reference to the largest deviations [7–10].

We also investigated the plots of excess molar refraction for all studied mixtures, at 298.15 K (see Fig. 2). The molar refractions of ME + DEA, ME + TEA,

TABLE IV Experimental refractive index (n_D) and deviations refractive index (Δn_D) for 2-methoxyethanol (**1**) + propylamine (**2**) binary mixtures

x_1	ϕ_1	n_D				Δn_D			
		288.15 K	*291.15* K	*293.15* K	*298.15* K	*288.15* K	*291.15* K	*293.15* K	*298.15* K
0.0000	0.0000	1.39134	1.38944	1.38818	1.38503	0.00000	0.00000	0.00000	0.00000
0.0502	0.0840	1.39391	1.39194	1.39058	1.38727	0.00149	0.00136	0.00123	0.00096
0.1009	0.1630	1.39608	1.39410	1.39278	1.38949	0.00265	0.00246	0.00233	0.00199
0.1501	0.2346	1.39793	1.39603	1.39475	1.39156	0.00359	0.00342	0.00330	0.00297
0.2002	0.3029	1.39966	1.39783	1.39656	1.39349	0.00444	0.00429	0.00416	0.00386
0.2504	0.3670	1.40123	1.39945	1.39820	1.39522	0.00519	0.00505	0.00491	0.00462
0.3000	0.4266	1.40269	1.40090	1.39965	1.39673	0.00589	0.00569	0.00553	0.00522
0.3498	0.4829	1.40392	1.40219	1.40093	1.39803	0.00640	0.00622	0.00602	0.00567
0.3997	0.5361	1.40502	1.40330	1.40204	1.39917	0.00682	0.00661	0.00639	0.00600
0.4499	0.5867	1.40594	1.40423	1.40296	1.40014	0.00709	0.00686	0.00661	0.00620
0.4998	0.6343	1.40665	1.40496	1.40372	1.40094	0.00719	0.00694	0.00670	0.00628
0.5504	0.6800	1.40715	1.40549	1.40429	1.40159	0.00711	0.00686	0.00664	0.00624
0.6000	0.7225	1.40745	1.40583	1.40467	1.40208	0.00686	0.00662	0.00643	0.00608
0.6498	0.7631	1.40756	1.40599	1.40487	1.40238	0.00645	0.00623	0.00606	0.00577
0.6999	0.8019	1.40749	1.40597	1.40489	1.40250	0.00589	0.00569	0.00554	0.00530
0.7495	0.8385	1.40728	1.40580	1.40474	1.40242	0.00521	0.00502	0.00488	0.00466
0.8000	0.8741	1.40696	1.40549	1.40443	1.40214	0.00443	0.00423	0.00407	0.00384
0.8511	0.9084	1.40651	1.40504	1.40396	1.40168	0.00354	0.00332	0.00313	0.00286
0.8999	0.9398	1.40596	1.40351	1.40341	1.40115	0.00259	0.00236	0.00214	0.00185
0.9499	0.9705	1.40522	1.40383	1.40278	1.40060	0.00146	0.00127	0.00108	0.00084
1.0000	1.0000	1.40414	1.40296	1.40211	1.40021	0.00000	0.00000	0.00000	0.00000

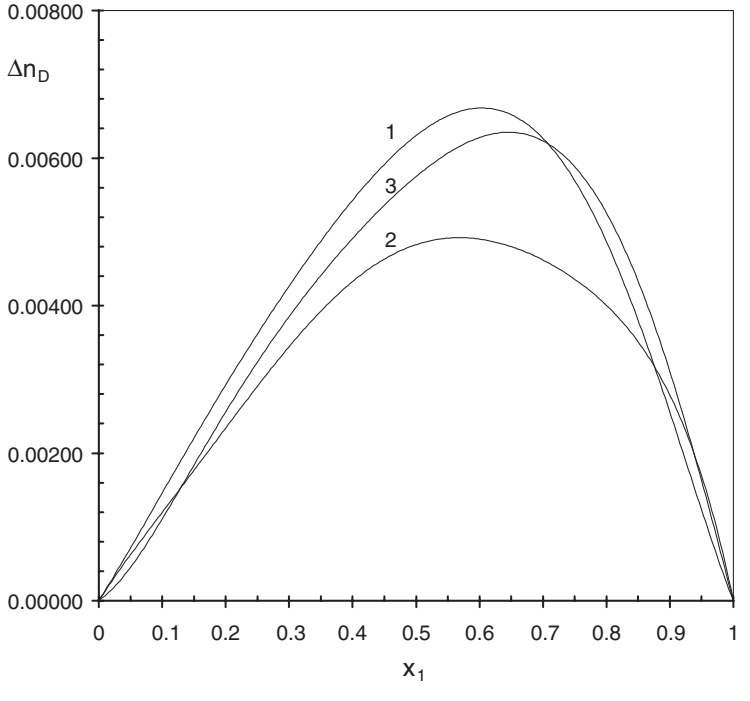

FIGURE 1 Plot of Δn as a function of composition for ME + DEA (**1**), ME + TEA (**2**), and ME + PA (**3**), at 298.15 K.

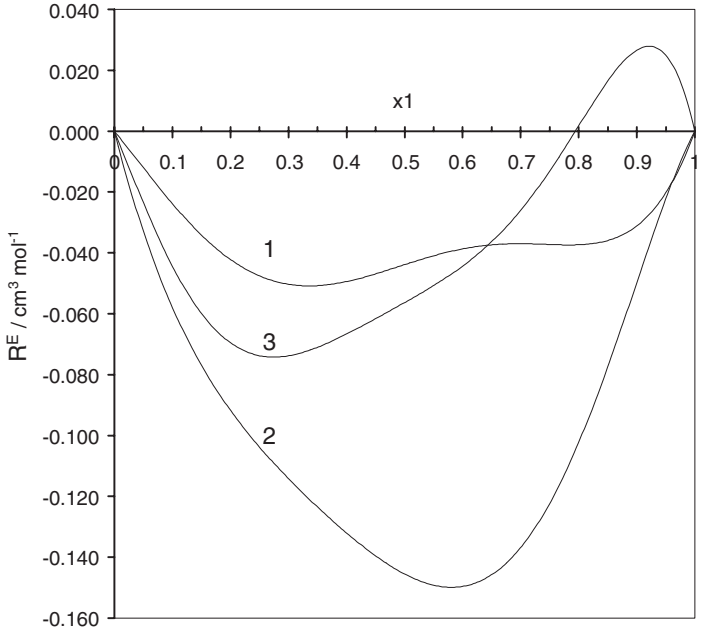

FIGURE 2 Plot of R^E as a function of composition for ME + DEA (**1**), ME + TEA (**2**), and ME + PA (**3**), at 298.15 K.

and ME + PA have been calculated from the refractive indices by the Lorentz–Lorenz equation:

$$R = (n^2 - 1) \cdot (x_1 \cdot M_1 + x_2 \cdot M_2)/(n_2 + 2) \cdot \rho \tag{3}$$

where ρ is the density [6,7], n is the refractive index, and x_i and M_i represent the mole fraction and molar mass of component i, respectively. The values of molar refraction of the studied binary mixtures, at 298.15 K, are given in Table V.

The R data for the mixtures have been used to calculate the excess molar refraction (R^E) using:

$$R^E = R - (x_1 \cdot R_1 + x_2 \cdot R_2) \tag{4}$$

The variations of R^E *versus* the mole fraction of 2-methoxyethanol (x_1) are presented in Fig. 2. The curves have been obtained by fitting the R^E values with a Redlich–Kister equation of the type [17]:

$$R^E = x_1 \cdot (1 - x_1) \sum_{j=0}^{4} a_j \cdot (2x_1 - 1)^j \tag{5}$$

Figure 2 shows that the excess of the molar refraction are negative for each binary system, with a minimum lying always nearly at $x_1 \approx 0.35$ for ME with diethylamine

TABLE V Molar refraction for ME + DEA, ME + TEA, and ME + PA binary mixtures, at 298.15 K

ME + DEA		*ME + TEA*		*ME + PA*	
x_1	R ($cm^3\,mol^{-1}$)	x_1	R ($cm^3\,mol^{-1}$)	x_1	R ($cm^3\,mol^{-1}$)
0.0000	24.3341	0.0000	34.3791	0.0000	19.4519
0.0500	24.0650	0.0500	33.5885	0.0502	19.4181
0.1000	23.8016	0.1020	32.7741	0.1009	19.3827
0.1499	23.5302	0.1502	32.0253	0.1501	19.3565
0.2001	23.2687	0.2001	31.2550	0.2002	19.3358
0.2500	23.0080	0.3011	29.6993	0.2504	19.3205
0.3000	22.7509	0.3501	28.9477	0.3000	19.3091
0.3498	22.4943	0.4005	28.1740	0.3498	19.2996
0.4000	22.2393	0.4508	27.4068	0.3997	19.2924
0.4498	21.9855	0.5002	26.6516	0.4499	19.2855
0.4995	21.7357	0.5503	25.8887	0.4998	19.2791
0.5500	21.4801	0.5998	25.1374	0.5504	19.2731
0.5999	21.2258	0.6499	24.3804	0.6000	19.2678
0.6495	20.9746	0.6995	23.6374	0.6498	19.2648
0.7000	20.7174	0.7498	22.8894	0.6999	19.2646
0.7500	20.4618	0.7992	22.1601	0.7495	19.2656
0.8000	20.2055	0.8504	21.4123	0.8000	19.2673
0.8501	19.9509	0.8998	20.6935	0.8511	19.2693
0.8998	19.7010	0.9499	19.9496	0.8999	19.2691
0.9500	19.4525	1.0000	19.2195	0.9499	19.2585
1.0000	19.2195			1.0000	19.2196

and propylamine, and $x_1 \approx 0.60$ for ME with triethylamine. As suggested by other authors [15,16,18,19], 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 their relative thermostability. The position of the relative minima in the plots of R^E *versus* x_1, could be taken as the true composition of these intermolecular complexes.

The results obtained in this work indicate that the respective stable intermolecular complexes of the ME · DEA, ME · TEA, ME · PA, ME · 2DEA, 3ME · 2TEA, and ME · 2PA types would be formed in the binary mixtures we have studied in this investigation.

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