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DENSITIES AND RELATIVE PERMITTIVITIES FOR MIXTURES OF 2-METHOXYETHANOL WITH DEA AND TEA, AT VARIOUS TEMPERATURES

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Abstract

Densities (ρ) and relative permittivities (ε) of numerous binary mixtures of 2-methoxyethanol (ME) (**1**)+diethylamine (DEA) (**2**) at four temperatures and 2-methoxyethanol (**1**)+triethylamine (TEA) (**2**) at five temperatures, between (291.15 and 313.15) K, are reported. These results are used to calculate excess molar volumes, and deviations in the relative permittivities. The results are fitted to the Redlich–Kister polynomial equation to estimate the binary coefficients and standard errors. Furthermore, the experimental results are used to disclose the nature of binary interactions in the bulk of studied the binary mixtures.

Keywords: diethylamine, intermolecular interactions, 2-methoxyethanol, physicochemical properties, triethylamine

Introduction

Systematic studies on intermolecular interactions and the internal structures of uniform binary liquid mixtures are still continued to be an area of interest in physical chemistry. Regarding structural studies, a review of the relevant literature shows that for the analysis of this type of effect in liquid solvent mixtures, it is possible to apply a wide range of spectral methods, thermochemical methods, as well as studies on the intensive macroscopic properties of solutions (such as relative permittivity, density, viscosity, etc.) carried out at different temperatures [1–2].

As a part of our experimental program on the measurements of physicochemical properties of binary liquid mixtures, we present here the densities and relative permittivities for the 2-methoxyethanol+diethylamine, at (291.15, 293.15, 298.15 and 303.15 K), and 2-methoxyethanol+triethylamine, at (293.15, 298.15, 303.15, 308.15 and 313.15 K), over the entire whole mole fraction ranges. We calculated the excess molar volumes, which were fitted to the Redlich–Kister equation [3].

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Experimental section

Materials

2-methoxyethanol (ME), diethylamine (DEA) and triethylamine (TEA) Merck, pro-analysis, containing less than 0.05% (mass/mass) of water, respectively (determined by Karl–Fischer method), were used. 2-methoxyethanol, diethylamine and triethylamine were further purified by the methods reported by Piekarski and Tkaczyk [7] and Riddick *et al.* [8]. The densities and relative permittivities for the pure solvents, at 298.15 K, were in a good agreement with the literature values (Table 1). The mixtures were prepared by weighing with an accuracy $\pm 1\cdot 10^{-4}$ 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 $1\cdot 10^{-4}$. All the liquids were stored in a dry-box over P_2O_5, and were degassed by ultrasounds just before the experiments.

Table 1 Reference density and relative permittivity values for pure 2-methoxyethanol, diethylamine and triethylamine, at 298.15 K

Solvent	ρ/g cm^{-3}		ε	
	this work	lit.	this work	lit.
2-methoxyethanol	0.96029	0.960288 [9]	16.96	16.94 [1]
Diethylamine	0.69895	0.69978 [10]	3.33 (at 293.14 K)	3.894 [8] (at 293.15 K)
Triethylamine	0.72485	0.72226 [11]	2.46 (at 293.15 K)	2.423 [8] (at 293.15 K)

Measurements

Solvent densities were measured with a bicapillary type Lipkin pycnometer, with a capacity of ca. 90 cm^3. Redistilled, deionized and degassed water with a specific conductance of $1\cdot 10^{-7}$ Ω^{-1} cm^{-1} was used for the calibration. The maximum error in the density measurements was $4\cdot 10^{-5}$ g cm^{-3}.

The relative permittivity measurements were carried out at 3 MHz, using a bridge of the OH-301 type (Radelkis, Hungary). The thermostatic stainless steel measuring cell was of the C3 ($1<\varepsilon<25$) type. The cell was calibrated with standard pure liquids, such as acetone, butan-1-ol and dichloromethane. All these solvents were of a spectrograde quality or higher. The relative permittivities for the standards were found in the literature [1, 8]. The uncertainty in the relative permittivity measurements was ±0.02.

In all measurements of the physical properties, a Haake model DC-30 thermostat was used at a constant digital temperature control of ±0.01 K.

Results and discussion

The experimental data of densities (ρ) and relative permittivities (ε) obtained from the measurements for the pure solvents and the analysed binary mixtures, at all the temperatures studied, are summarized in Tables 2 and 3.

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

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

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 those of the mixtures at different temperatures, respectively. The denotion **1** always corresponds to 2-methoxyethanol.

The deviation of the relative permittivity from a mole fraction average was calculated by:

$$\Delta\varepsilon=\varepsilon-(x_1\varepsilon_1+x_2\varepsilon_2) \tag{2}$$

where ε_1, ε_2 and ε are the relative permittivities of the pure species (**1** and **2**), and that of the mixtures at different temperatures, respectively.

The excess volumes and deviations from the relative permittivities were fitted by a Redlich–Kister type equation:

$$V^E/\mathrm{cm^3\ mol^{-1}}\ \text{or}\quad \Delta\varepsilon=x_1(1-x_1)\sum_{j=0}^{k}a_j(2x_2-1)^j \tag{3}$$

The parameters a_j of Eq. (3) were evaluated by the least-squares method. The values of these parameters, at each temperature studied, with standard deviations $\sigma(V^E)$ and $\sigma(\Delta\varepsilon)$, are summarized in Tables 4–6.

The standard deviation values were obtained from

$$\sigma=\left[\frac{\sum(X_{\mathrm{exptl}}-X_{\mathrm{calcd}}}{N-p}\right]^{1/2} \tag{4}$$

where N is the number of experimental points, p is the number of parameters, X_{exptl} and X_{calcd} are the experimental and calculated properties, respectively.

The variations of V^E and $\Delta\varepsilon$ *vs.* the mole fraction of 2-methoxyethanol (x_1) at 298.15 K are presented in Figs 1–2, respectively. Figure 1 shows that the excess molar volumes are negative for all the investigated systems, with a minimum positioned always nearly $x_1\approx0.5$ for ME–DEA, and nearly $x_1\approx0.6$ for ME–TEA binary mixtures. The magnitude of the volume concentration follows the sequence: diethylamine>triethylamine. Moreover, the excess volumes were found to increase with the increasing temperature (Tables 4 and 5). 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 the –OH groups in 2-methoxyethanol and the nitrogen atoms in the two amines. Another effect, which would give a

Table 2 Experimental densities and relative permittivities for 2-methoxyethanol (**1**)+diethylamine (**2**) binary mixtures

x_1	T/K				T/K			
	291.15	293.15	298.15	303.15	291.15	293.15	298.15	303.15
	ρ/g cm^{-1}				ε			
0.0000	0.70664	0.70436	0.69895	0.69389	3.36	3.33	3.12	2.93
0.0500	0.71931	0.71688	0.71140	0.70626	3.73	3.70	3.56	3.46
0.1001	0.73210	0.72956	0.72403	0.71885	4.14	4.11	4.00	3.90
0.1499	0.74494	0.74234	0.73678	0.73156	4.58	4.55	4.45	4.33
0.2001	0.75791	0.75529	0.74971	0.74447	5.07	5.03	4.92	4.79
0.2500	0.77085	0.76823	0.76265	0.75738	5.59	5.57	5.43	5.29
0.3000	0.78385	0.78124	0.77567	0.77039	6.17	6.12	5.97	5.83
0.3498	0.79682	0.79423	0.78867	0.78339	6.78	6.71	6.54	6.39
0.4001	0.80990	0.80733	0.80179	0.79650	7.44	7.36	7.19	7.00
0.4498	0.82289	0.82032	0.81482	0.80953	8.14	8.03	7.86	7.64
0.4995	0.83587	0.83329	0.82780	0.82254	8.87	8.74	8.58	8.35
0.5499	0.84905	0.84644	0.84101	0.83577	9.64	9.51	9.33	9.08
0.5998	0.86206	0.85945	0.85405	0.84883	10.45	10.32	10.13	9.85
0.6495	0.87500	0.87236	0.86701	0.86183	11.28	11.15	10.97	10.65
0.7000	0.88815	0.88552	0.88022	0.87509	12.15	12.01	11.80	11.54
0.7501	0.90120	0.89857	0.89334	0.88827	13.04	12.88	12.66	12.38
0.8000	0.91422	0.91165	0.90651	0.90151	13.95	13.79	13.54	13.26
0.8501	0.92729	0.92482	0.91978	0.91487	14.86	14.70	14.43	14.12
0.9000	0.94033	0.93803	0.93311	0.92830	15.77	15.60	15.31	14.98
0.9500	0.95341	0.95138	0.94661	0.94192	16.66	16.48	16.16	15.81
1.0000	0.96652	0.96488	0.96029	0.95576	17.58	17.35	16.96	16.55

Table 3 Experimental densities and relative permittivities for 2-methoxyethanol (**1**)+triethylamine (**2**) binary mixtures

x_1	T/K					T/K				
	291.15	293.15	298.15	303.15	313.15	291.15	293.15	298.15	303.15	308.15
	ρ/g cm^{-1}					ε				
0.0000	0.73026	0.72485	0.71944	0.71403	0.70863	2.50	2.46	2.42	2.41	2.39
0.0501	0.73884	0.73326	0.72782	0.72231	0.71679	3.07	3.05	3.04	3.05	3.05
0.1020	0.74793	0.74230	0.73682	0.73127	0.72560	3.45	3.43	3.40	3.40	3.40
0.1502	0.75656	0.75092	0.74541	0.73985	0.73410	3.78	3.74	3.68	3.66	3.64
0.2001	0.76576	0.76012	0.75461	0.74905	0.74323	4.03	3.97	3.90	3.86	3.82
0.2504	0.77533	0.76972	0.76419	0.75864	0.75280	4.31	4.24	4.16	4.11	4.04
0.3011	0.78532	0.77972	0.77420	0.76866	0.76283	4.61	4.54	4.45	4.38	4.29
0.3501	0.79530	0.78974	0.78421	0.77870	0.77288	4.92	4.86	4.77	4.69	4.57
0.4005	0.80594	0.80041	0.79488	0.78938	0.78361	5.28	5.21	5.12	5.03	4.90
0.4508	0.81696	0.81145	0.80592	0.80044	0.79472	5.67	5.60	5.52	5.41	5.27
0.5002	0.82816	0.82267	0.81714	0.81168	0.80603	6.10	6.04	5.95	5.81	5.67
0.5503	0.83992	0.83445	0.82894	0.82348	0.81791	6.63	6.55	6.46	6.31	6.15
0.5998	0.85195	0.84650	0.84100	0.83552	0.83005	7.26	7.15	7.05	6.87	6.70
0.6499	0.86454	0.85912	0.85363	0.84820	0.84280	8.05	7.92	7.79	7.59	7.41
0.6995	0.87742	0.87202	0.86657	0.86117	0.85586	8.99	8.86	8.69	8.46	8.26
0.7498	0.89091	0.88556	0.88017	0.87480	0.86959	10.21	10.06	9.86	9.60	9.38
0.7992	0.90458	0.89930	0.89399	0.888869	0.88358	11.53	11.36	11.12	10.84	10.60
0.8504	0.91922	0.91403	0.90885	0.90364	0.89865	13.14	12.97	12.68	12.38	12.10
0.8992	0.93363	0.92858	0.92355	0.91847	0.91358	14.72	14.54	14.21	13.90	13.58
0.9510	0.94943	0.94458	0.93976	0.93488	0.93013	16.31	16.12	15.77	15.42	15.06
1.0000	0.96488	0.96029	0.95576	0.95110	0.94654	17.58	17.35	16.96	16.55	16.15

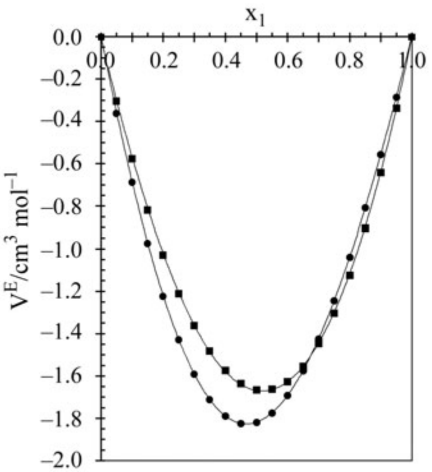

Fig. 1 Plot of V^E as a function of composition for ● – 2-methoxyethanol+diethylamine and ■ – 2-methoxyethanol+triethylamine, at 298.15 K

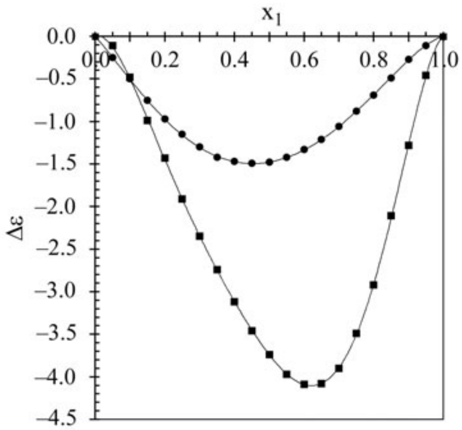

Fig. 2 Plot of Δε as a function of composition for ● – 2-methoxyethanol+diethylamine and ■ – 2-methoxyethanol+triethylamine, at 298.15 K

negative contribution to the excess 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. In the mixtures studied the ME, DEA and TEA molecules have different molar volumes as pure species:

$$V^E(\mathrm{ME})=79.242\ \mathrm{cm}^3\ \mathrm{mol}^{-1}<V^E(\mathrm{DEA})=207.601\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$$
$$<V^E(\mathrm{TEA})=288.531\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$$

therefore this effect should be significant and of great importance. The difference in the free volumes between 2-methoxyethanol and the two amines would facilitate the penetration of one component (ME) into the others (amines). The discussed effect is confirmed by the obtained in the present paper courses of the changes of V^E values (Fig. 1, Tables 4 and 5).

Table 4 Parameters a_j in Eq. (3), and standard deviations $\sigma(V^E)$ and $\sigma(\Delta\varepsilon)$ for 2-methoxyethanol+diethylamine

	a_0	a_1	a_2	a_3	σ
			T=291.15 K		
V^E/cm^3 mol^{-1}	–7.4492	0.8958	0.2025	–0.0917	0.001
$\Delta\varepsilon$	–6.3991	1.8115	1.0291	–0.1307	0.006
			T=293.15 K		
V^E/cm^3 mol^{-1}	–7.2811	1.0164	0.6150	–0.1802	0.001
$\Delta\varepsilon$	–6.3228	1.7141	1.5692	0.0099	0.005
			T=298.15 K		
V^E/cm^3 mol^{-1}	–7.2728	1.0241	0.7244	–0.2082	0.001
$\Delta\varepsilon$	–5.8620	1.8317	2.3502	–0.3679	0.008
			T=303.15 K		
V^E/cm^3 mol^{-1}	–7.2434	1.0427	0.7917	–0.2394	0.001
$\Delta\varepsilon$	–5.6217	1.5635	3.4250	–0.3937	0.009

Table 5 Parameters a_j in Eq. (3), and standard deviations $\sigma(V^E)$ for 2-methoxyethanol+ triethylamine

T/K	a_0	a_1	a_2	a_3	σ/V^E
293.15	–6.6939	–0.8620	–0.4837	0.6505	0.003
298.15	–6.6643	–0.8395	–0.1385	0.4140	0.003
303.15	–6.5995	–0.7545	–0.0215	0.3994	0.003
308.15	–6.5842	–0.6938	0.2183	0.2268	0.003
313.15	–6.4549	–1.0344	0.4232	0.3193	0.003

Figure 2 shows that the relative permittivity deviations are also negative for each binary system, with a minimum lying always nearly $x_1\approx0.5$ for ME–DEA, and nearly $x_1\approx0.6$ for ME–TEA binary mixtures. As evidenced from the calculations, the relative permittivity deviations decrease with an increase in the temperature (Tables 4 and 6).

Table 6 Parameters a_j in Eq. (3), and standard deviations $\sigma(\Delta\varepsilon)$ for 2-methoxyethanol+ triethylamine

T/K	a_0	a_1	a_2	a_3	a_4	$\sigma/\Delta\varepsilon$
291.15	–15.7521	–11.1207	0.0308	9.1513	12.6904	0.013
293.15	–15.4970	–11.0709	–0.9135	9.0353	14.4711	0.014
298.15	–14.9741	–10.4708	–1.7772	7.9608	15.5811	0.014
303.15	–14.6518	–10.5163	–2.2438	8.0755	16.9300	0.014
308.15	–14.4155	–10.1239	–1.7217	7.2722	16.8851	0.014

As suggested by other authors [4–6], the study of this extrathermodynamic 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 $\Delta\varepsilon$ *vs*. x_1, could be taken as the true composition of these intermolecular complexes.

Conclusions

The results obtained in this work seem to indicate that the respective stable intermolecular complexes of the ME–DEA or 3ME–2TEA types would be formed in the studied binary mixtures of 2-methoxyethanol+diethylamine or 2-methoxyethanol+triethylamine.

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