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Densities and Relative Permittivities for 2-Methoxyethanol + Dioxane from (291.15 to 313.15) K

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Densities and relative permittivities of binary mixtures of 2-methoxyethanol + dioxane at five temperatures, between (291.15 and 313.15) K, are reported. Excess molar volumes are calculated.

Introduction

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 and/or temperature, are of great importance in our understanding of the nature of molecular aggregation that exists in the binary mixtures.

As a part of our experimental program on the measurement of physicochemical properties of binary liquid mixtures, we present here the densities and relative permittivities for 2-methoxyethanol + dioxane at (291.15, 293.15, 298.15, 303.15, and 308.15) K, over the mole fraction range. We calculated the excess molar volumes, which were fitted to the Redlich−Kister equation.[1]

Experimental Section

Materials. 2-Methoxyethanol and dioxane [Merck, pro-analysis, containing <0.05% (w/w) water, respectively (determined by Karl Fischer method)] were used. 2-Methoxyethanol and dioxane were further purified according to the methods described by Piekarski and Tkaczyk[2] and Riddick et al.[3] The densities and relative permittivities for the pure solvents, at 298.15 K, were in good agreement with literature values (Table 1).

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 was $< 1 \times 10^{-4}$.

Measurements. The relative permittivity measurements were carried out at 3 MHz, with an accuracy of ±0.1%, using a bridge of the type OH-301 (made in Radelcis, Hungary). The thermostatic stainless steel measuring cell was of C3 ($1 < \epsilon < 25$) type. The sample cell is of the covered coaxial capacitor type with vacuum capacitance of 2.5 pF (C3). The cell was calibrated with standard pure liquids, such as acetone, butan-1-ol, and dichloromethane. All of these solvents were of spectrograde quality or higher. The relative permittivities for the standards were taken from the literature.[3,4] Solvent densities were measured with a bicapillary type Lipkin pycnometer, with a capacity of ~90 cm^3. The maximum error in the density measurements was 4×10^{-5} g·cm^{-3}.

Each temperature was maintained with an accuracy of ±0.01 K.

Table 1. Reference Density and Relative Permittivity Values of 2-Methoxyethanol and Dioxane at 298.15 K

	ρ/g·cm^{-3}		ϵ	
solvent	this work	lit.	this work	lit.
2-methoxyethanol	0.96029	0.9601[5] 0.960288[6] 0.96024[4]	16.96	16.94[7]
dioxane	1.02789	1.02797[4] 1.0279[8]	2.21	2.209[4] 2.207[8]

Results and Discussion

The experimental data of density (ρ) and relative permittivity (ϵ) obtained from the measurements of the pure solvents and for the analyzed binary mixtures at all investigated temperatures are summarized in Table 2.

The first step of this study involves investigation of the dependence of density on temperature, and the following relationship was used:

$$\rho/\mathrm{g \cdot cm^{-3}} = \sum_{0}^{i} \alpha_i (T/{}^\circ C)^i \tag{1}$$

The α_i coefficients, for $i = 1$, are summarized in Table 3 together with standard deviations [$\sigma(\rho)$] for each mixture. Equation 1 reproduces the experimental ρ values with an average uncertainty, evaluated by means of the relationship

$$\delta\rho = \frac{1}{N} \sum_{N} |\rho^{\mathrm{calcd}} - \rho^{\mathrm{exptl}}| \tag{2}$$

where N is the number of experimental points.

The value of $\delta\rho$ is equal to ± 0.00002 g·cm^{-3} over the set of experimental ρ values (see Table 2).

In this paper, our investigations of dielectric behaviors as a function of temperature are given by

$$\ln \epsilon = \alpha_0^* + \alpha_i^* \times T/\mathrm{K} \tag{3}$$

where α_i^* ($i = 0, 1$) is an empirical constant.

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Table 2. Experimental Densities and Reletive Permittivities for 2-Methoxyethanol (1) + Dioxane (2) Binary Mixtures

	ρ/g·cm^{-3}					ϵ				
x_1	291.15 K	293.15 K	298.15 K	303.15 K	308.15 K	291.15 K	293.15 K	298.15 K	303.15 K	308.15 K
0.0000	1.03551	1.03340	1.02789	1.02129	1.01554	2.26	2.23	2.21	2.20	2.18
0.0508	1.03157	1.02953	1.02410	1.01764	1.01196	2.52	2.46	2.42	2.36	2.33
0.1006	1.02768	1.02568	1.02031	1.01402	1.00848	2.87	2.82	2.80	2.73	2.70
0.1509	1.02380	1.02184	1.01661	1.01045	1.00497	3.28	3.24	3.22	3.14	3.11
0.2015	1.01997	1.01805	1.01288	1.00683	1.00151	3.76	3.71	3.68	3.60	3.57
0.2496	1.01641	1.01452	1.00939	1.00347	0.99826	4.27	4.22	4.17	4.08	4.05
0.2998	1.01278	1.01091	1.00589	1.00010	0.99495	4.84	4.77	4.70	4.60	4.57
0.3510	1.00920	1.00736	1.00239	0.99674	0.99164	5.47	5.39	5.28	5.18	5.14
0.3995	1.00587	1.00405	0.99912	0.99361	0.98855	6.14	6.04	5.89	5.78	5.74
0.4503	1.00245	1.00064	0.99575	0.99037	0.98536	6.83	6.75	6.56	6.44	6.39
0.5006	0.99914	0.99734	0.99247	0.98719	0.98223	7.56	7.49	7.28	7.15	7.09
0.5504	0.99589	0.99412	0.98929	0.98407	0.97917	8.33	8.26	8.02	7.88	7.81
0.6007	0.99262	0.99086	0.98604	0.98092	0.97603	9.19	9.10	8.83	8.67	8.59
0.6496	0.98945	0.98772	0.98292	0.97787	0.97306	10.02	9.94	9.66	9.48	9.38
0.6998	0.98616	0.98446	0.97971	0.97474	0.96994	10.96	10.87	10.55	10.36	10.23
0.7502	0.98285	0.98118	0.97646	0.97158	0.96681	11.92	11.84	11.51	11.30	11.14
0.8004	0.97954	0.97788	0.97323	0.96842	0.96368	12.93	12.84	12.49	12.26	12.06
0.8511	0.97617	0.97453	0.96991	0.96523	0.96051	13.96	13.86	13.52	13.26	13.01
0.8999	0.97294	0.97133	0.96676	0.96214	0.95745	15.12	15.01	14.62	14.32	14.02
0.9503	0.96966	0.96804	0.96349	0.95892	0.95425	16.29	16.18	15.77	15.44	15.08
1.0000	0.96652	0.96488	0.96029	0.95576	0.95110	17.54	17.41	16.96	16.59	16.16

Table 3. Coefficients α_i and Standard Deviations $\sigma(\rho)$ of Equation 1 and Coefficients α_i^* and Standard Deviations $\sigma(\ln \epsilon)$ of Equation 3 for 2-Methoxyethanol (1) + Dioxane (2)

x_1	α_0	$\alpha_1 \times 10^4$	$10^5 \times \sigma(\rho)$/g·cm^{-3}	α_0^*	$\alpha_1^* \times 10^3$	$10^3 \times \sigma(\ln \epsilon)$
0.0000	1.381	−11.861	7	2.535	−6.014	6
0.0508	1.371	−11.649	4	2.195	−4.393	4
0.1006	1.360	−11.408	5	2.090	−3.452	3
0.1509	1.349	−11.179	5	2.090	−3.106	2
0.2015	1.340	−10.970	1	2.194	−2.996	2
0.2496	1.331	−10.788	3	2.360	−3.130	2
0.2998	1.321	−10.588	4	2.553	−3.368	3
0.3510	1.313	−10.421	4	2.758	−3.656	3
0.3995	1.305	−10.269	3	2.963	−3.966	4
0.4503	1.297	−10.124	2	3.089	−4.029	4
0.5006	1.291	−10.013	5	3.162	−3.924	3
0.5504	1.284	−9.904	3	3.269	−3.957	3
0.6007	1.279	−9.819	3	3.413	−4.117	4
0.6496	1.272	−9.707	4	3.479	−4.043	3
0.6998	1.266	−9.601	3	3.612	−4.192	3
0.7502	1.259	−9.492	1	3.677	−4.120	2
0.8004	1.253	−9.378	2	3.783	−4.204	2
0.8511	1.246	−9.249	4	3.860	−4.206	1
0.8999	1.239	−9.148	5	4.027	−4.504	1
0.9503	1.235	−9.094	3	4.126	−4.584	1
1.0000	1.233	−9.081	2	4.273	−4.835	1

Table 4. Coefficients c_j and Standard Deviations $\sigma(\ln \epsilon)$ of Equation 5 for 2-Methoxyethanol + Dioxane Binary Mixtures

T/K	c_0	c_1	c_2	c_3	$10^3 \times \sigma(\ln \epsilon)$
291.15	2.2251	5.1531	12.6297	−2.4708	1
293.15	2.1431	5.7340	10.3780	−0.8464	1
298.15	2.0766	6.4758	7.2385	1.1655	2
303.15	2.0225	6.2931	7.4819	0.7935	1
308.15	2.0010	6.1634	8.0114	−0.0142	2

Table 5. Coefficients a_j and Standard Deviations $\sigma(V_m^E)$ of Equation 7 for 2-Methoxyethanol + Dioxane Binary Mixtures

T/K	a_0	a_1	a_2	a_3	$10^3 \times \sigma(V_m^E)$/cm^3·mol^{-1}
291.15	1.0404	−0.5491	0.0301	0.5221	1
293.15	1.0152	−0.5269	−0.0211	0.4784	1
298.15	0.9640	−0.4693	−0.0504	0.3516	2
303.15	0.8861	−0.4663	−0.0308	0.3038	3
308.15	0.8027	−0.4089	−0.0343	0.2216	1

The α_i^* coefficients of this fitting procedure are listed in Table 3, along with the standard deviations $\sigma(\ln \epsilon)$ for each solvent system.

Equation 3 reproduces the experimental ϵ values with an average uncertainty, evaluated by means of

$$\delta\epsilon = \frac{1}{N}\sum_N |\epsilon^{\text{calcd}} - \epsilon^{\text{exptl}}| \qquad (4)$$

where N is the number of experimental points and $\delta\epsilon = \pm 0.03$ (see Table 2).

The variation of relative permittivity with binary composition was analyzed by using the equation

$$\ln \epsilon = \sum_0^j c_j x_1^j \qquad (5)$$

which could be fitted to the experimental data at each temperature using a least-squares method. The values of c_j coefficients, for $j = 3$, and the standard deviations $\sigma(\ln \epsilon)$ are summarized in Table 4. This equation reproduces the experimental data of ϵ (see Table 2) with $\delta\epsilon = \pm 0.04$.

From the measured densities (see Table 2) the excess values of molar volumes (V_m^E) of the mixtures, at each investigated temperature, were fitted in the equation

$$V_m^E = x_1 M_1(\rho^{-1} - \rho_1^{\circ -1}) + x_2 M_2(\rho^{-1} - \rho_2^{\circ -1}) \qquad (6)$$

where M_i is the molar mass of component i.

The excess values of molar volumes (V_m^E) values have been fitted in a Redlich–Kister equation of the type

$$V_m^E = x_1 x_2 \sum_{j=0}^{k} a_j (2x_2 - 1)^j \qquad (7)$$

The parameters a_j of eq 7 were evaluated by the method of least-squares and are listed in Table 5 along with standard deviations $\sigma(V_m^E)$. The results of V_m^E calculations for the investigated systems, at 298.15 K, are presented in graphic form in Figure 1.

V_m^E is positive over the whole composition range (and all of the measured temperatures—see Table 5), and it has an absolute maximum at $x_1 \approx 0.40$.

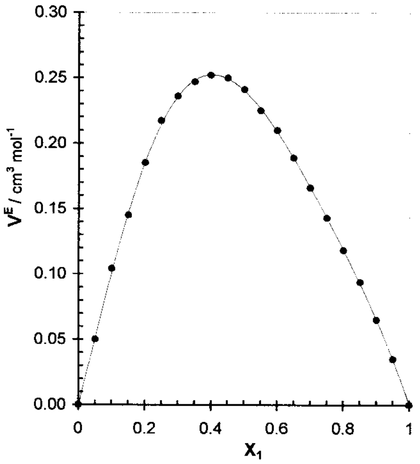

Figure 1. Excess molar volumes (V_m^E) for 2-methoxyethanol (1)–dioxane (2) at 298.15 K.

The positive V_m^E over the entire range of mole fraction may be attributed to the association between unlike molecules, 2-methoxyethanol and dioxane, through hydrogen bond formation and enhancement of 2-methoxyethanol + dioxane interactions.

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