Density, Relative Permittivity, and Viscosity at Various Temperatures for 2-Methoxyethanol + Propylamine Mixtures

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Densities (ρ) and relative permittivities (ϵ) at four temperatures, between (288.15 and 298.15) K, and viscosities (η) at three temperatures, between (291.15 and 298.15) K, of binary mixtures of 2-methoxyethanol (1) + propylamine (2) are reported. The excess molar volumes (V^E) and the relative permittivity and viscosity deviations ($\Delta\epsilon$ and $\Delta\eta$) were calculated from these experimental data. The results are discussed in terms of intermolecular interactions.

Introduction

Previously we have investigated the internal structure in liquid binary mixtures in which 2-methoxyethanol or an aprotic solvent is one of the two constituents, on the basis of the correlation existing between the ^{1}H NMR spectral results and some physicochemical intensive properties of the same binary mixtures.[1−4]

Continuing our work on solution properties, we present in this work the density, relative permittivity, and viscosity of binary mixtures of 2-methoxyethanol (ME) + propylamine (PA), at (288.15, 291.15, 293.15, and 298.15) K. We calculated the excesses molar volumes and the relative permittivity and viscosity deviations, which were fitted to the Redlich−Kister equation.[5]

Experimental Section

Materials. 2-Methoxyethanol and propylamine (Merck, pro-analysis), containing less than 0.05% (w/w) water, respectively (determined by the Karl Fischer method), were used.

2-Methoxyethanol and propylamine were further purified by the methods described by Piekarski[6] and Góralski.[7] The mixtures were prepared by mass, with weighings accurate 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 a drybox over phosphoric pentoxide and degassed by ultrasound just before the experiment.

Experimental data of densities, relative permittivities, and viscosities for the pure solvents, at 298.15 K, are compared with values available in the literature and listed in Table 1.

Measurements. The relative permittivity measurements were carried out at 3 MHz 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 cell was calibrated with standard pure liquids, such as acetone, butan-1-ol, and dichloromethane. All these solvent were of spectrograde quality or higher. The relative permittivities for the standards were taken from the literature.[8,9] The accuracy in the relative permittivity measurements was ±0.02.

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 3×10^{-5} g·cm^{-3}.

The flow times of the mixtures and the pure liquids were measured in a ViscoClock (made by Schott), equipped with an Ubbelohde capillary viscometer. The viscometer was calibrated with conductivity water. The time measurement tolerance was ±0.005%, and the display accuracy was ±0.01 s. The accuracy in the viscosity measurements was ±0.01 mPa·s.

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

Results and Discussion

The experimental values of density (ρ), relative permittivity (ϵ) at (288.15, 291.15, 293.15, and 298.15) K, and viscosity (η) at (291.15, 293.15, and 298.15) K are given in Tables 2 and 3. From the measured densities (see Table 2) the excess values of molar volumes V^E of the mixtures, at the each investigated temperature, were fitted to the equation[16]

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

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. The values of V^E of the binary mixtures, at 298.15 K, are shown graphically in Figure 1.

The deviation of the viscosity from a mole fraction average was calculated from the following equation[16,17]

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \qquad (2)$$

where η_1, η_2, and η are the viscosities of 2-methoxyethanol, propylamine, and the mixtures, respectively. The values of $\Delta\eta$ of the binary mixtures are shown graphically in Figure 3.

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

	ρ/g·cm^{-3}		ϵ		η/mPa·s	
solvent	this work	lit.	this work	lit.	this work	lit.
2-methoxyethanol	0.960 29	0.960 24[9] 0.960 1[10] 0.960 288[11]	16.98	16.94[12]	1.544	1.5414[13]
propylamine	0.712 12	0.710 69[7] 0.712 3[14] 0.710 86[15]	5.11	5.08[8]	0.342	0.353[8]

Table 2. Experimental Density and Relative Permittivity for 2-Methoxyethanol (1) + Propylamine (2) Binary Mixtures

	ρ/g·cm^{-3} at T/K =				ϵ at T/K =			
x_1	288.15	291.15	293.15	298.15	288.15	291.15	293.15	298.15
0.0000	0.718 76	0.718 24	0.717 19	0.712 12	5.73	5.55	5.42	5.11
0.0502	0.733 96	0.732 98	0.731 69	0.726 48	6.20	6.03	5.91	5.62
0.1009	0.748 86	0.747 67	0.746 35	0.741 12	6.76	6.59	6.48	6.19
0.1501	0.762 92	0.761 65	0.760 35	0.755 12	7.34	7.17	7.06	6.76
0.2002	0.776 88	0.775 58	0.774 31	0.769 12	7.97	7.81	7.70	7.36
0.2504	0.790 54	0.789 23	0.787 97	0.782 76	8.66	8.48	8.36	8.03
0.3000	0.803 78	0.802 44	0.801 17	0.795 93	9.30	9.11	8.99	8.65
0.3498	0.816 87	0.815 49	0.814 18	0.808 95	10.06	9.84	9.67	9.30
0.3997	0.829 81	0.828 38	0.827 01	0.821 68	10.80	10.58	10.38	9.98
0.4499	0.842 69	0.841 16	0.839 73	0.834 38	11.55	11.31	11.08	10.65
0.4998	0.855 33	0.853 70	0.852 21	0.846 96	12.28	12.05	11.79	11.32
0.5504	0.867 94	0.866 21	0.864 67	0.859 46	13.02	12.79	12.50	11.99
0.6000	0.880 09	0.878 21	0.876 63	0.871 48	13.73	13.48	13.18	12.65
0.6498	0.891 99	0.889 96	0.888 34	0.883 26	14.41	14.15	13.84	13.29
0.6999	0.903 63	0.901 43	0.899 76	0.894 70	15.05	14.79	14.48	13.91
0.7495	0.914 78	0.912 41	0.910 68	0.905 67	15.67	15.39	15.08	14.50
0.8000	0.925 80	0.923 22	0.921 44	0.916 49	16.23	15.95	15.65	15.08
0.8511	0.936 68	0.933 92	0.932 06	0.927 12	16.73	16.45	16.18	15.61
0.8999	0.946 99	0.944 10	0.942 21	0.937 12	17.15	16.88	16.65	16.10
0.9499	0.957 80	0.954 86	0.953 04	0.948 23	17.52	17.25	17.06	16.56
1.0000	0.969 25	0.966 52	0.964 88	0.960 29	17.79	17.54	17.41	16.98

Table 3. Experimental Viscosity for 2-Methoxyethanol (1) + Propylamine (2) Binary Mixtures

	η/mPa·s at T/K =				η/mPa·s at T/K =		
x_1	291.15	293.15	298.15	x_1	291.15	293.15	298.15
0.0000	0.383	0.359	0.342	0.5504	1.202	1.149	1.039
0.0502	0.417	0.396	0.380	0.6000	1.301	1.241	1.116
0.1009	0.453	0.435	0.415	0.6498	1.391	1.325	1.186
0.1501	0.496	0.479	0.453	0.6999	1.470	1.400	1.249
0.2002	0.551	0.533	0.501	0.7495	1.535	1.462	1.304
0.2504	0.617	0.599	0.559	0.8000	1.588	1.515	1.354
0.3000	0.696	0.674	0.627	0.8511	1.632	1.561	1.400
0.3498	0.785	0.759	0.703	0.8999	1.668	1.601	1.443
0.3997	0.884	0.852	0.785	0.9499	1.709	1.647	1.490
0.4499	0.989	0.950	0.870	1.0000	1.765	1.708	1.544
0.4998	1.095	1.050	0.955				

The deviation of the relative permittivity from a mole fraction average was calculated from the equation[16]

$$\Delta\epsilon = \epsilon - (x_1\epsilon_1 + x_2\epsilon_2) \quad (3)$$

where ϵ_1, ϵ_2, and ϵ are the relative permittivities of 2-methoxyethanol, propylamine, and the mixtures, respectively. The values of $\Delta\epsilon$ of the binary mixtures are shown graphically in Figure 2.

Excess volume and deviations of relative permittivity and viscosity were fitted by a Redlich−Kister type equation[5]

$$V^E/\text{cm}^3\cdot\text{mol}^{-1} \text{ or } \Delta\epsilon \text{ or } \Delta\eta/\text{mPa}\cdot\text{s} = x_1(1-x_1)\sum_{j=0}^{k} a_j(2x_2-1)^j \quad (4)$$

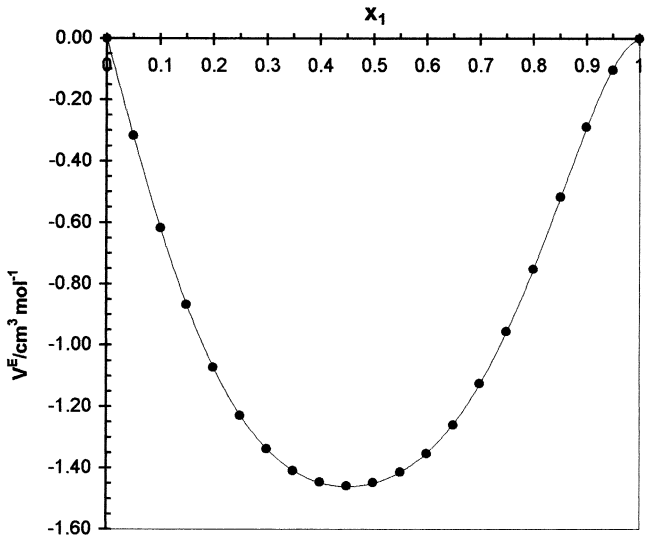

Figure 1. Excess molar volumes (V^E) for 2-methoxyethanol (1) + propylamine (2), at 298.15 K.

The parameters a_j of eq 4 were evaluated by the least-squares method. The values of these parameters, at each studied temperature, with standard deviation σ, are summarized in Table 4.

Standard deviation values were obtained from

$$\sigma = \left[\frac{\sum(X_{\text{exptl}} - X_{\text{calcd}})^2}{n-p}\right]^{1/2} \quad (5)$$

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

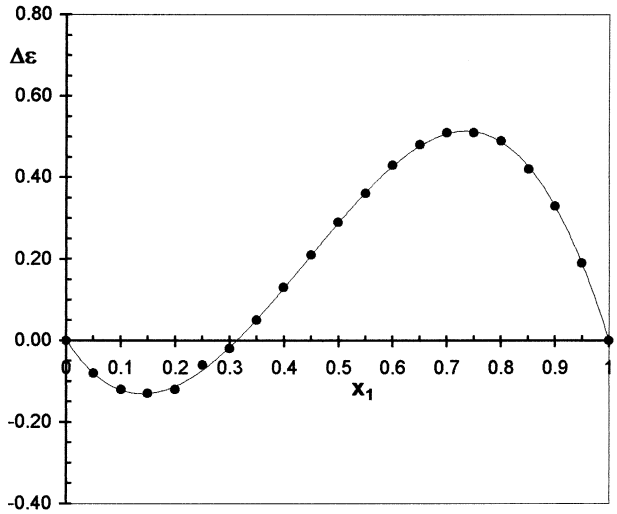

Figure 2. Deviations of relative permittivity ($\Delta\epsilon$) for 2-methoxyethanol (1) + propylamine (2), at 298.15 K.

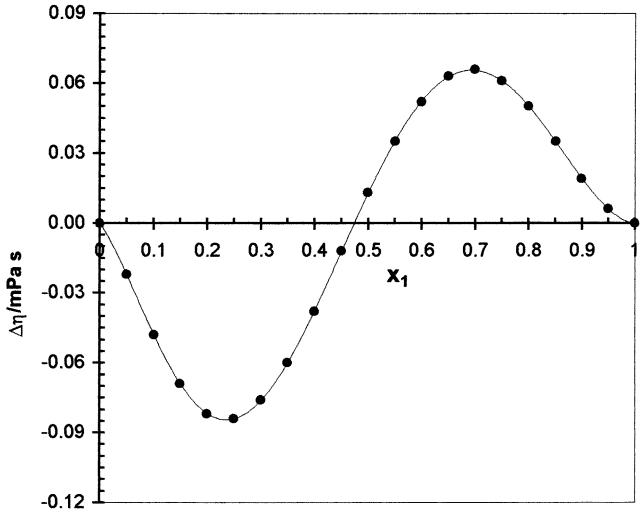

Figure 3. Deviations of viscosity ($\Delta\eta$) for 2-methoxyethanol (1) + propylamine (2), at 298.15 K.

Table 4. Parameters a_j of Eq 4 and Standard Deviations σ

	a_0	a_1	a_2	a_3	σ
		$T = 288.15$ K			
V^E/cm^3·mol^{-1}	−5.9621	0.8667	−0.1270	2.2329	0.011
$\Delta\epsilon$	2.0823	5.3904	0.0614	−0.1672	0.012
		$T = 291.15$ K			
V^E/cm^3·mol^{-1}	−5.9381	0.8512	0.5058	2.0676	0.016
$\Delta\epsilon$	2.0207	5.1969	0.0554	−0.4838	0.013
$\Delta\eta$/mPa·s	0.0936	1.5067	−0.3589	−1.1649	0.001
		$T = 293.15$ K			
V^E/cm^3·mol^{-1}	−5.9164	0.9564	0.7784	1.9249	0.021
$\Delta\epsilon$	1.5232	4.0695	0.1668	−0.0563	0.011
$\Delta\eta$/mPa·s	0.0715	1.2735	−0.3726	−1.0292	0.001
		$T = 298.15$ K			
V^E/cm^3·mol^{-1}	−5.8997	0.9312	0.8909	2.0402	0.025
$\Delta\epsilon$	1.1636	3.1184	0.0079	0.0040	0.005
$\Delta\eta$/mPa·s	0.0419	0.9711	−0.3579	−0.7919	0.002

Figure 1 shows that the excess molar volumes (V^E) are negative over the whole composition range (and for all measured temperatures; see Table 4), and it has an absolute minimum at $x_1 \approx 0.50$.

For 2-methoxyethanol + propylamine the deviation of relative permittivity values is illustrated by the S-shaped curve, with minimum and maximum at ~0.15 and 0.70 mole fraction of 2-methoxyethanol, respectively (Figure 2). The trend in the viscosity deviation values is similar to that of the deviation of the relative permittivity values, as can be seen in Figure 3 and Table 4, with the minimum near $x_1 \approx 0.25$ and the maximum near $x_1 \approx 0.70$.

The negative values of V^E and the course of changes of $\Delta\epsilon$ and $\Delta\eta$ over the entire range of mole fraction may be attributed mainly to the association through intermolecular hydrogen bonds between the −OH group of 2-methoxyethanol and the $-NH_2$ group of propylamine.

Obtained results seem to indicate that stable intermolecular complexes of ME·PA, ME·3PA, and 2ME·PA types are respectively formed in the studied binary mixtures of 2-methoxyethanol + propylamine.

Literature Cited

(1) Kinart, C. M.; Kinart, W. J.; Ćwiklińska, A. 2-Methoxyethanol−Acetonitrile Binary Mixtures and Their Physicochemical Properties. *Phys. Chem. Liq.* **2001**, *39*, 589−605.

(2) Kinart, C. M.; Kinart, W. J.; Ćwiklińska, A. Densities and Relative Permittivities for 2- Methoxyethanol + Dioxane from (291.15 to 313.15) K. *J. Chem. Eng. Data*. **2002**, *47*, 23−25.

(3) Kinart, C. M.; Kinart, W. J.; Ćwiklińska, A. Density and Viscosity at Various Temperatures for 2-Methoxyethanol + Acetone Mixtures. *J. Chem. Eng. Data.* **2002**, *47*, 76−78.

(4) Kinart, C. M.; Kinart, W. J.; Ćwiklińska, A. 2-Methoxyethanol−Tetrahydrofuran Binary Liquid System. *J. Therm. Anal. Calorim.* **2002**, *68*, 307−317.

(5) Redlich, O.; Kister, A. T. Thermodynamics of nonelectrolyte solutions. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ing. Eng. Chem.* **1948**, *40*, 345−348.

(6) Piekarski, H.; Tkaczyk, M. Thermochemical Properties of Electrolyte Solutions in 2-Alkoxyethanol−Water Mixtures. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2299−2306.

(7) Góralski, P.; Wasiak, M.; Bald, A. Heat Capacities, Speeds of Sound, and Isothermal Compressibilities of Some n-Amines and Tri-n-amines at 298.15 K. *J. Chem. Eng. Data.* **2002**, *47*, 83−86.

(8) Riddick, J. B.; Bunger, W. B.; Sakano, T. K. *Organic Solvents. Physical Properties and Methods of Purification*; J. Wiley Publ.: New York, 1986.

(9) Cocchi, M.; De Benedetti, P.; Seeber, R.; Tassi, L.; Ulrici, A. Development of Quantitative Structure−Property Relationships Using Calculated Descriptors for the Prediction of the Physicochemical Properties (n_D, ρ, bp, ϵ, η) of a Series of Organic Solvents. *J. Chem. Inf. Comput. Sci.* **1999**, *39*, 1190−1203.

(10) Albuquerque, L.; Ventura, C.; Goncalves, R. Refractive Indices, Densities and Excess Propertries for Binary Mixtures Containing Methanol, Ethanol, 1,2-Ethanediol and 2- Methoxyethanol. *J. Chem. Eng. Data.* **1996**, *41*, 685−688.

(11) Tassi, L. Ionic Association of Alkali-metal Bromides in 2-Metoxyethanol. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 733−738.

(12) Franchini, G. C.; Marchetti, A.; Tagliazucchi, M.; Tassi, L.; Tosi, G. Etanae-1,2-diol + 2-Methoxyethanol Solvent System. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2583−2588.

(13) Das, B.; Hazra, D. K. Viscosities and excess molar volumes for 2-methoxy-1-ethanol + water at different temperatures. *J. Chem. Eng. Data* **1993**, *38*, 361−363.

(14) Vogel, A. J. Physical Properties and Chemical Constitution. Part XXII. Primary, secondary, and tertiary amines. *J. Chem. Soc.* **1948**, 1825−1833.

(15) Letcher, T. M. Thermodynamics of mixtures containing aliphatic amines. II. Excess volumes of primary or secondary or tertiary aliphatic amines with benzene and substituted benzene compounds. *J. Thermodyn.* **1972**, *4*, 159−173.

(16) Glasstone, S.; Laidler, J. K.; Eyring, H. *The Theory of Rate Processes*; McGraw-Hill: New York, 1941.

(17) Ausländer, G. The properties of mixtures. Part I. *Br. Chem. Eng.* **1964**, *9*, 66−93.

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