Relative Permittivity, Viscosity, and Speed of Sound for 2-Methoxyethanol + Butylamine Mixtures

Cezary M. Kinart,*,† Wojciech J. Kinart,‡ and Dorota Chęcińska-Majak†

Department of Chemistry, University of Łodź, 90-236 Łodź, Pomorska 163, Poland, and Department of Organic Chemistry, University of Łodź, 90-136 Łodź, Narutowicza 68, Poland

Relative permittivities (ϵ) at five temperatures, between (293.15 and 313.15) K, viscosities (η) at three temperatures, between (293.15 and 303.15) K, and speeds of sound (u) at 298.15 K of binary mixtures of 2-methoxyethanol (1) + butylamine (2) are reported. From all those data, the deviations from mole fraction additivity of the relative permittivity ($\Delta\epsilon$), viscosity ($\Delta\eta$), and speed of sound (Δu) were calculated and fitted to a Redlich−Kister equation.

Introduction

In our laboratory, the thermodynamic properties of binary mixtures of 2-methoxyethanol with organic solvents have been extensively studied with the aim of investigating the intermolecular interactions and the internal structure of mixed binary solvents.[1−4]

In continuation of our program on the thermodynamic, acoustic, dielectric, and transport properties of some mixtures of 2-methoxyethanol with amines,[4] the present paper reports relative permittivity, viscosity, and speed of sound for binary mixtures containing 2-methoxyethanol with butylamine at various temperatures. We calculated deviations from a mole fraction average of the relative permittivity, viscosity, and speed of sound, which were fitted to the Redlich−Kister equation.[5]

Experimental Section

Materials. 2-Methoxyethanol and butylamine, Merck, pro-analysis, containing less than 0.05 mass % of water, respectively (determined by Karl Fischer method), were used.

2-Methoxyethanol and butylamine were further purified by the methods described by Piekarski[6] and Góralski.[7] The mixtures were prepared by mass with the accuracy $\pm 1 \times 10^{-4}$ 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 $< 1 \times 10^{-4}$. All the liquids were stored in a drybox over P_2O_5 and were degassed by ultrasound just before the experiments.

Measurements. The relative permittivity measurements were carried out at 3 MHz using a bridge of the OH-301 type (Radelcis, Hungary). The thermostatic stainless steel measuring cell was of the C3 ($1 < \epsilon < 25$) 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.[8,9] The accuracy in the relative permittivity measurements was ±0.02.

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 ±0.003 mPa·s.

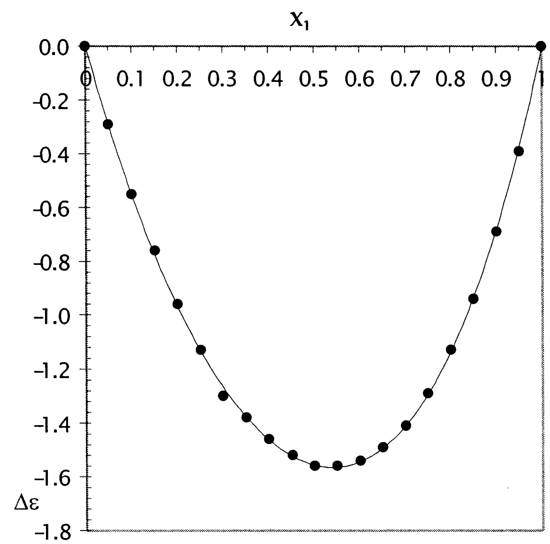

Figure 1. Deviations of relative permittivity ($\Delta\epsilon$) for 2-methoxyethanol (1) + butylamine (2), at 298.15 K.

The speeds of sound were measured using an MPFU velocimeter (Ecolab, Poland). The device was calibrated with water by its procedure, and the uncertainty in measurement can be estimated as ± 0.5 m·s^{-1}. Values of speed of sound at 298.15 K were calculated by interpolation from the linear $u = f(T)$ function in the temperature range 298.00 K to 298.30 K.

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

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

Results and Discussion

The experimental values of relative permittivities (ϵ) at (293.15, 298.15, 303.15, 308.15, and 313.15) K, viscosities

* To whom correspondence should be addressed. E-mail: ckinart@krysia.uni.lodz.pl.
† Department of Chemistry.
‡ Department of Organic Chemistry.

10.1021/je030127e CCC: $25.00 © 2003 American Chemical Society
Published on Web 05/14/2003

Table 1. Reference Relative Permittivity, Viscosity, and Speed of Sound Values of 2-Methoxyethanol and Butylamine, at 298.15 K

	u/m·s^{-1}		ϵ		η/mPa·s	
solvent	this work	lit.	this work	lit.	this work	lit.
2-methoxyethanol	1344.5	1332.0[12]	16.98	16.94[15]	1.544	1.5414[16]
butylamine	1251.6	1249.8[7] 1259.0[13] 1247.8[14]	4.91	4.88[8]	0.467 (at 303.15 K)	0.464[17] (at 303.15 K)

Table 2. Experimental Relative Permittivity, Viscosity, and Speed of Sound for 2-Methoxyethanol (1) + Butylamine (2) Binary Mixtures

	ϵ					η/mPa·s			u/m·s^{-1}
x_1	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	293.15 K	298.15 K	303.15 K	298.15 K
0.0000	4.91	4.62	4.48	4.33	4.21	0.525	0.496	0.467	1251.6
0.0501	4.77	4.54	4.45	4.31	4.25	0.566	0.536	0.504	1257.0
0.0999	4.90	4.67	4.61	4.47	4.43	0.613	0.578	0.544	1262.3
0.1508	5.20	4.97	4.91	4.78	4.74	0.669	0.625	0.588	1267.7
0.2001	5.66	5.40	5.34	5.22	5.15	0.731	0.680	0.636	1273.1
0.2509	6.23	5.95	5.88	5.75	5.65	0.801	0.743	0.691	1278.4
0.3000	6.82	6.53	6.46	6.32	6.21	0.879	0.810	0.750	1283.6
0.3498	7.47	7.24	7.14	6.99	6.81	0.964	0.886	0.815	1288.8
0.4001	8.19	7.97	7.84	7.68	7.50	1.053	0.966	0.885	1294.0
0.4511	8.95	8.74	8.57	8.42	8.22	1.146	1.049	0.957	1299.1
0.5001	9.70	9.48	9.29	9.13	8.93	1.238	1.133	1.031	1304.0
0.5496	10.46	10.24	10.02	9.86	9.64	1.327	1.214	1.103	1308.8
0.5997	11.24	11.01	10.79	10.58	10.36	1.412	1.290	1.170	1313.5
0.6503	12.02	11.75	11.53	11.31	11.08	1.488	1.358	1.232	1318.1
0.7000	12.78	12.49	12.24	12.01	11.78	1.552	1.415	1.286	1322.4
0.7492	13.54	13.22	12.94	12.69	12.46	1.604	1.461	1.327	1326.6
0.7999	14.31	13.94	13.66	13.38	13.13	1.643	1.493	1.359	1330.7
0.8491	15.03	14.65	14.34	14.05	13.79	1.671	1.516	1.379	1334.5
0.8993	15.79	15.39	15.08	14.74	14.45	1.686	1.525	1.389	1338.0
0.9500	16.57	16.16	15.82	15.45	15.12	1.696	1.533	1.395	1341.4
1.0000	17.41	16.96	16.59	16.16	15.78	1.708	1.544	1.404	1344.5

(η) at (293.15, 298.15, and 303.15) K, and speeds of sound at 298.15 K are summarized in Table 2.

The deviation of the relative permittivity from a mole fraction average was calculated from the equation[10,11]

$$\Delta\epsilon = \epsilon - (x_1\epsilon_1 + x_2\epsilon_2) \qquad (1)$$

where ϵ_1, ϵ_2, and ϵ are the relative permittivities of 2-methoxyethanol and butylamine and those of the mixtures, respectively. The values of $\Delta\epsilon$ of the binary mixtures are shown graphically in Figure 1.

The deviation of the viscosity from a mole fraction average was calculated from the following equation[10,11]

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

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

The deviation of the speed of sound from a mole fraction average was calculated from the following equation[10,11]

$$\Delta u = u - (x_1u_1 + x_2u_2) \qquad (3)$$

where u_1, u_2, and u are the speeds of sound in 2-methoxyethanol, butylamine, and their mixtures, respectively. The values of Δu of the binary mixtures are shown graphically in Figure 3.

Deviations of relative permittivity, viscosity, and speed of sound were fitted by a Redlich−Kister type equation[5]

$$\Delta\epsilon/\text{cm}^3\cdot\text{mol}^{-1} \quad \text{or} \quad \Delta\eta/\text{mPa}\cdot\text{s}$$

$$\text{oro}\Delta u/\text{m}\cdot\text{s}^{-1} = x_1(1-x_1)\sum_{j=0}^{k} a_j(2x_2-1)^j \qquad (4)$$

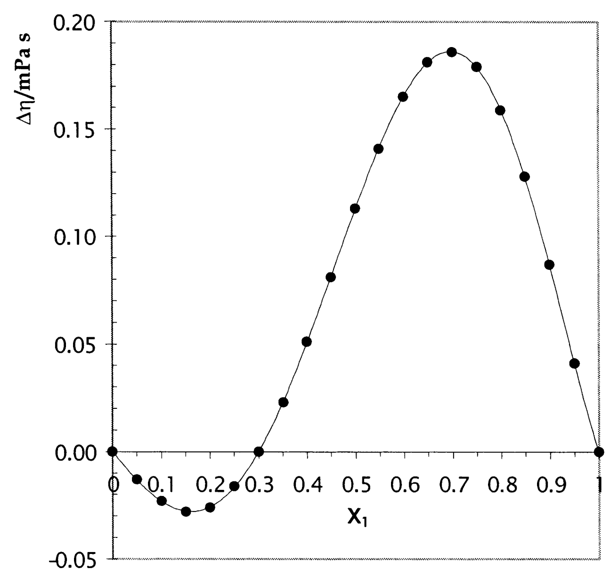

Figure 2. Deviations of viscosity ($\Delta\eta$) for 2-methoxyethanol (1) + butylamine (2), at 298.15 K.

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 3.

The standard deviation values were obtained from

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

where n is the number of experimental points, p is the number of parameters, and X_{exp} and X_{cal} are the experimental and calculated properties, respectively.

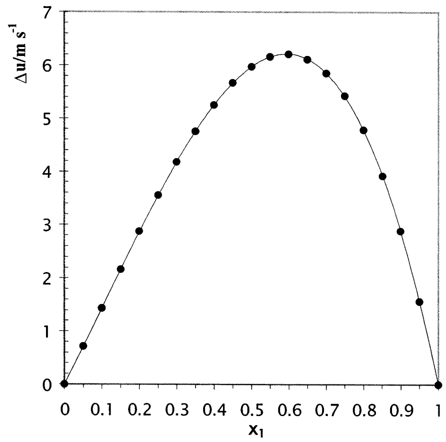

Figure 3. Deviations of speed of sound (Δu) for 2-methoxyethanol (1) + butylamine (2), at 298.15 K.

Table 3. Parameters a_j of Eq 3 and Standard Deviations $\sigma(\Delta\epsilon)$, $\sigma(\Delta\eta)$, and $\sigma(\Delta u)$ for 2-Methoxyethanol + Butylamine

	a_0	a_1	a_2	a_3	a_4	σ
			T/K = 293.15			
$\Delta\epsilon$	−5.8794	5.5996	−3.1588	1.0685	−2.8425	0.0094
$\Delta\eta$/mPa·s	0.4842	1.2961	−0.0427	−0.6603	−0.2169	0.0004
			T/K = 298.15			
$\Delta\epsilon$	−5.2340	6.0033	−5.0330	−0.0971	0.1717	0.0073
$\Delta\eta$/mPa·s	0.4501	1.2225	−0.0112	−0.7232	−0.2250	0.0004
Δu/m·s^{-1}	23.8835	9.9821	−0.0780	−0.1265	−0.0297	0.0075
			T/K = 303.15			
$\Delta\epsilon$	−4.9609	5.4980	−4.1100	0.0071	−0.2285	0.0094
$\Delta\eta$/mPa·s	0.3786	1.0531	0.1249	−0.6098	−0.2854	0.0003
			T/K = 308.15			
$\Delta\epsilon$	−4.4595	5.6387	−4.0959	−0.0073	0.1112	0.0050
			T/K = 313.15			
$\Delta\epsilon$	−4.3093	5.7312	−2.9491	−0.5711	0.2808	0.0077

Figure 1 shows that all $\Delta\epsilon$ values are negative and that they become less negative when temperature decreases (see Table 3), with a minimum lying always nearly $x_1 \approx 0.30$.

As suggested by other authors,[15,18] the study of this structural parameter for binary liquid systems represents a unique tool for investigating the formation of intermolecular complexes, and it provides a valuable aid for determining their stoichiometry and their relative thermostability. The position of the relative minima in the plots of $\Delta\epsilon$ versus x_1 could be taken as the true composition of these intermolecular complexes.

For 2-methoxyethanol + butylamine the deviation of viscosity values is illustrated by the S-shaped curve (for all measured temperatures—see Table 3), with minimum and maximum at ~0.15 and 0.70 mole fraction of 2-methoxyethanol, respectively (Figure 2).

The deviation of speed of sound (see Figure 3) shows that all Δu values are positive with a maximum lying nearly $x_1 \approx 0.60$.

After taking into consideration opinions of many researchers, it is necessary to assume that, at the composition range of liquid mixtures of 2-methoxyethanol + butylamine where $\Delta\eta$ and Δu are displaying maximum values, the stable intermolecular complexes are formed.[11−14]

The results obtained in this work seem to indicate that the respective stable intermolecular complexes of the ME·2n-BA, 2ME·n-BA, or 3ME·2n-BA types would be formed in the studied binary mixtures of 2-methoxyethanol (ME) + butylamine (n-BA).

Literature Cited

(1) 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.

(2) 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.

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

(4) Kinart, C. M.; Kinart, W. J.; Chęcińska-Majak, D. Density, Relative Permittivity, and Viscosity at Various Temperatures for 2-Methoxyethanol + Propylamine. *J. Chem. Eng. Data* **2002**, *47*, 1537−1539.

(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*; John Wiley Publ.: New York, 1986.

(9) 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.

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

(11) Kinart, C. M.; Kinart, W. J. Review Article. Physicochemical Methods Used to Study Internal Structures of Liquid Binary Mixtures. *Phys. Chem. Liq*. **2000**, *38*, 155−180.

(12) Aminabhavi, T. M.; Gopalakrishna, B. Density, Viscosity, Refractive Index, and Speed of Sound in Aqueous Mixtures of *N,N*-Dimethylformamide, Dimethyl Sulfoxide, *N,N*-Dimethylacetamide, Acetonitrile, Ethylene Glycol, Diethylene Glycol, 1,4-Dioxan, Tetrahydrofuran, 2-Methoxyethanol, and 2-Ethoxyethanol at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 856−861.

(13) Patil, K. J. Ultrasonic Sound Velocity Behaviour in Organic Polar Liquids. *Ind. J. Pure Appl. Phys.* **1978**, *16*, 608−613.

(14) Dominguez, M.; Lopez, M. C.; Santafe, J.; Royo, F. M.; Urieta, J. S. Densities, Speeds of Sound, and Isentropic Compressibilities of Binary and Ternary Mixtures Containing $CH_3(CH_2)_3OH$, CH_3-$(CH_2)CH_3$ and $CH_3(CH_2)_3NH_2$ at Temperature of 298.15 K. *J. Chem. Thermodyn*. **1997**, *29*, 99−109.

(15) 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.

(16) 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.

(17) Weng, W. L. Densities and Viscosities for Binary Mixtures of Butylamine with Aliphatic Alcohols. *J. Chem. Eng. Data* **2000**, *45*, 606−609.

(18) Awwad, Akl M.; Al.-Dujaili, A. H.; Syriagh, S. R. Dielectric studies of binary mixtures of N-formylmorpholine and an aromatic hydrocarbon. Comparison with theory. *J. Mol. Liq*. **2002**, *100*, 129−141.

Received for review February 3, 2003. Accepted April 7, 2003.

JE030127E