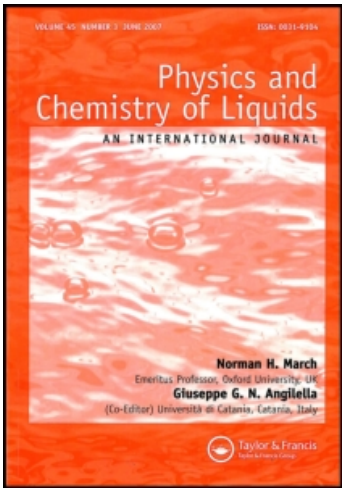

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Density, relative permittivity, viscosity and speed of sound for 2-methoxyethanol + isobutylamine mixtures

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Density, relative permittivity, viscosity and speed of sound for 2-methoxyethanol + isobutylamine mixtures

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Densities (ρ), relative permittivities (ε), viscosities (η), and speeds of sound (u) at 298.15 K of binary mixtures of 2-methoxyethanol (**1**) + isobutylamine (**2**), are reported. From all those data, the excess molar volumes, and deviations from mole fraction additivity of the relative permittivity ($\Delta\varepsilon$), viscosity ($\Delta\eta$), speed of sound (Δu), and isentropic compressibility ($\Delta\kappa$) have been calculated. The results for V^{E}, $\Delta\varepsilon$, $\Delta\ln\eta$, Δu, and $\Delta\kappa$ are discussed on the basis of intermolecular interactions between the components of the analysed mixtures.

Keywords: Density; Relative permittivity; Viscosity; Speed of sound; 2-Methoxyethanol; Isobutylamine

1. Introduction

In earlier papers, we reported the thermodynamic and physicochemical properties of binary mixtures of 2-methoxyethanol with aliphatic amines at different temperatures [1–4]. These results suggested the relative importance of the hydrogen-bonding interactions between the 2-methoxyethanol and aliphatic amine molecules. In continuation of these investigations, the present article reports the density, relative permittivity, viscosity, and speed of sound for binary mixtures containing 2-methoxyethanol (ME) with isobutylamine (i-BA) over the whole concentration range at 298.15 K.

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2. Experimental

2.1. *Materials*

2-Methoxyethanol and isobutylamine, Merck, pro-analysis, containing less than 0.05 mass % of water, respectively (determined by Karl–Fischer method), were used. 2-Methoxyethanol and isobutylamine were further purified by the methods described by Riddick [5]. The mixtures were prepared, just before use, by mass on a Sartorius balance of the type ING1, operating in a dry box to avoid atmospheric moisture. Conversion to molar quantities was based on the relative atomic mass table published in 1985, next issued by IUPAC in 1986. The error in the mole fraction 2-methoxyethanol is estimated to be less than $\pm 1 \times 10^{-4}$. All the liquids were stored in a dry-box over P_2O_5, and were degassed by ultrasounds just before the experiments.

2.2. *Measurements*

The densities were determined by means of a bicapillary type Lipkin pycnometer, with a capacity of ca 90 cm^3. Double distilled, deionized, and degassed water with a specific conductance of $1 \times 10^{-7}\,\Omega^{-1}\,cm^{-1}$ was used for the calibration. The maximum error in the density measurements was $\pm 1 \times 10^{-5}\,g\,cm^{-3}$.

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 ($1 < \varepsilon < 25$) type. The cell was calibrated with standard pure liquids, such as acetone, butan-1-ol and dichloromethane. All these solvents were of a spectro-grade quality or higher. The relative permittivity for the standards was found in the literature [5]. The accuracy in the relative permittivity measurements was ±0.02.

The flow times of the mixtures and pure liquids were measured in a ViscoClock (made by Schott), equipped with an Ubbelohde capillary viscometer. Double distilled, deionized, and degassed water with a specific conductance of $1 \times 10^{-7}\,\Omega^{-1}\,cm^{-1}$ was used for the calibration. The time measurement tolerance was ±0.005%, and the display accuracy was ±0.01 s. The accuracy in the viscosity measurements was $\pm 0.001\,mPa\,s^{-1}$.

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

3. Results and discussion

The experimental values of densities (ρ), relative permittivities (ε), viscosities (η), and speeds of sound at 298.15 K are summarized in table 1.

From the measured densities, the excess molar volumes V^E of the mixtures were calculated from the equation:

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

Table 1. Experimental density, relative permittivity, viscosity, and speed of sound for 2-methoxyethanol (**1**) + isobutylamine (**2**) binary mixtures, at 298.15 K.

x_1	ρ (g cm^{-3})	ε	ε (mPa s^{-1})	u (m s^{-1})
0.0000	0.72968	4.43	0.563	1214.5
0.0500	0.74078	4.71	0.614	1222.6
0.1001	0.75199	5.05	0.666	1230.6
0.1511	0.76346	5.48	0.719	1238.3
0.2000	0.77450	5.95	0.788	1245.6
0.2513	0.78613	6.48	0.869	1253.2
0.2996	0.79712	7.02	0.950	1260.2
0.3519	0.80907	7.66	1.043	1267.7
0.4002	0.82014	8.28	1.132	1274.6
0.4491	0.83139	8.94	1.221	1281.3
0.4989	0.84288	9.63	1.308	1287.7
0.5501	0.85473	10.36	1.387	1294.1
0.6000	0.86632	11.09	1.457	1299.9
0.6521	0.87845	11.86	1.520	1305.8
0.6999	0.88961	12.57	1.567	1311.1
0.7502	0.90138	13.33	1.608	1316.4
0.8000	0.91307	14.06	1.632	1321.8
0.8512	0.92511	14.83	1.643	1327.5
0.9000	0.93663	15.54	1.641	1333.0
0.9492	0.94827	16.24	1.609	1338.7
1.0000	0.96029	16.96	1.544	1344.5

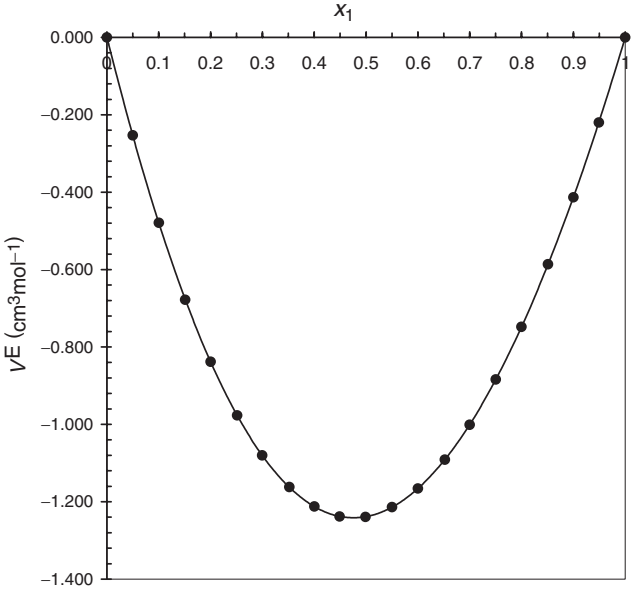

Figure 1. Plot of excess molar volume (V^E) against mole fraction ME for ME + i-BA binary liquid mixtures, at $T = 298.15$ K.

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 298.15 K, respectively. The values of $\Delta\varepsilon$ of the binary mixtures are shown graphically in figure 1.

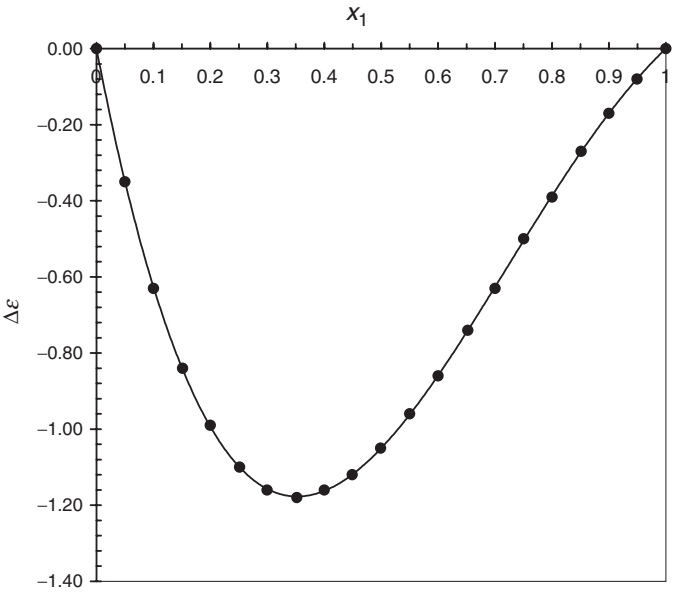

Figure 2. Plot of deviation relative permittivity ($\Delta\varepsilon$) against mole fraction ME for ME + i-BA binary liquid mixtures, at $T = 298.15$ K.

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

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

where ε_1, ε_2, and ε are the relative permittivities of the 2-methoxyethanol, isobutylamine, and those of the mixtures, respectively. The values of $\Delta\varepsilon$ of the binary mixtures are shown graphically in figure 2.

The deviation of the viscosity from a mole fraction average was calculated from the following equation:

$$\Delta \ln \eta = \ln \eta - (x_1 \cdot \ln \eta_1 + x_2 \cdot \ln \eta_2) \tag{3}$$

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

From these experimental data and values of speed of sound and density, the deviations in the speed of sound (Δu) and isentropic compressibility ($\Delta\kappa$) from a mole fraction average were calculated from the following equation:

$$\Delta u = u - (x_1 u_1 + x_2 u_2) \tag{4}$$

$$\Delta\kappa = \frac{1}{u^2\rho} - \left(x_1 \cdot \frac{1}{u_1^2\rho_1} - x_2 \cdot \frac{1}{u_2^2\rho_2}\right) \tag{5}$$

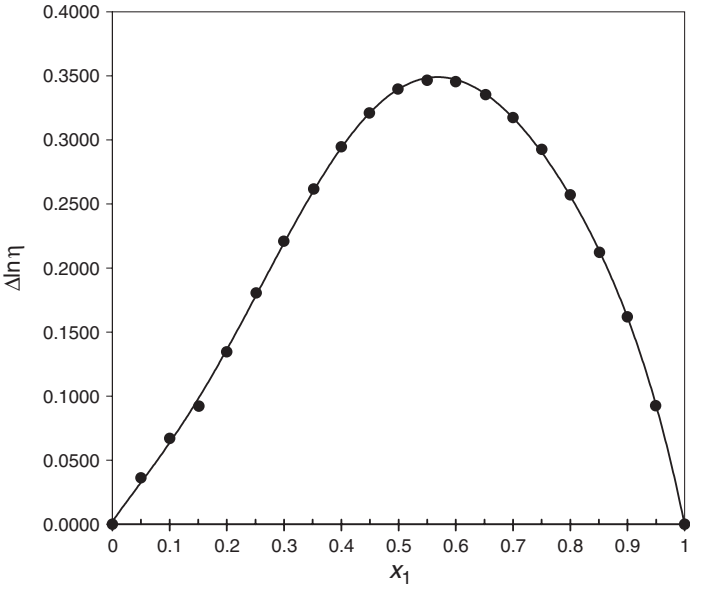

Figure 3. Plot of $\Delta \ln \eta$ against mole fraction ME for ME + i-BA binary liquid mixtures, at $T = 298.15\,\mathrm{K}$.

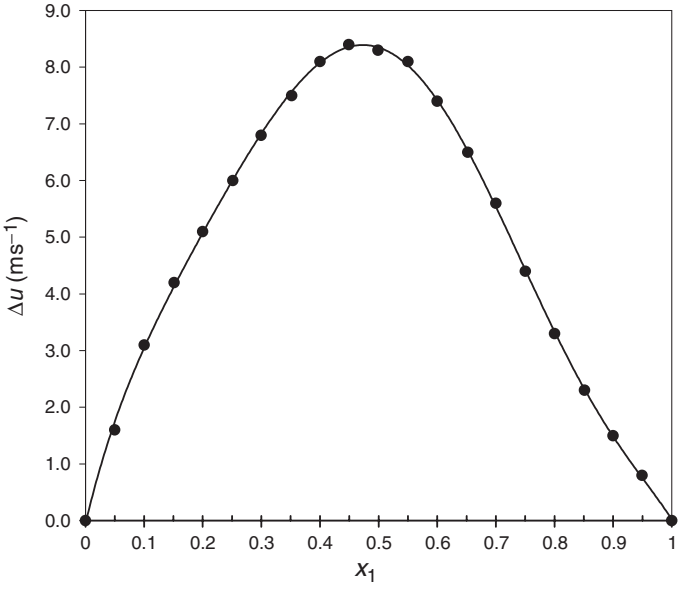

Figure 4. Plot of deviation speed of sound (Δu) against mole fraction ME for ME + i-BA binary liquid mixtures, at $T = 298.15\,\mathrm{K}$.

where u_1, u_2, u and ρ_1, ρ_2, ρ are the speeds of sound and densities in 2-methoxyethanol (**1**), isobutylamine (**2**), and their mixtures, respectively.

The values of Δu and $\Delta \kappa$ of the binary mixtures are shown graphically in figures 4 and 5.

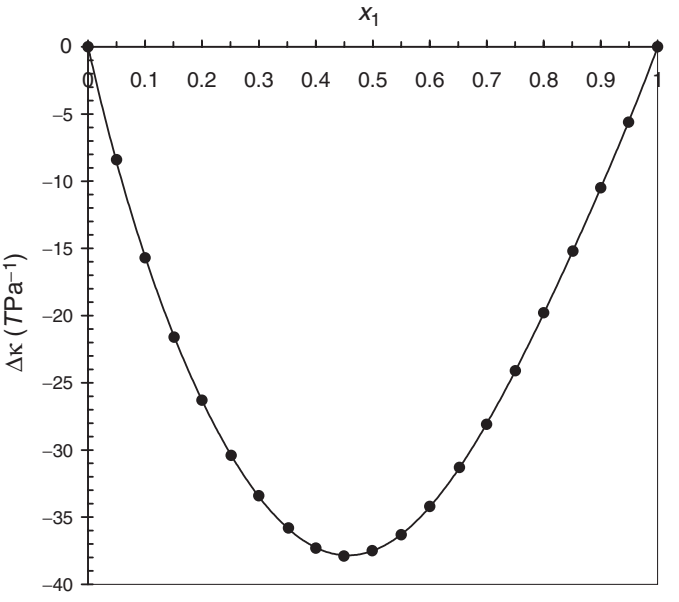

Figure 5. Plot of deviation isentropic compressibility ($\Delta\kappa$) against mole fraction ME for ME + i-BA binary liquid mixtures, at $T = 298.15$ K.

Table 2. Parameters a_j of equation (3) and standard deviations $\sigma(V^E)$, $\sigma(\Delta\varepsilon)$, $\sigma(\Delta\ln\eta)$, $\sigma(\Delta u)$, and $\sigma(\Delta\kappa)$ for 2-methoxyethanol + isobutylamine binary mixtures at 298.15 K.

Function	a_0	a_1	a_2	a_3	σ
2-Methoxyethanol + isobutylamine					
V^E ($cm^3\,mol^{-1}$)	−4.9545	0.4855	−0.0018	−0.0470	0.001
$\Delta\varepsilon$	−4.1958	3.1603	−0.3395	0.0072	0.003
$\Delta\ln\eta$	1.3377	0.5486	−0.2352	0.2062	0.006
Δu ($m\,s^{-1}$)	32.5752	−6.2833	−15.1430	−7.1981	0.222
$\Delta\kappa$ ($T\,Pa^{-1}$)	−149.0829	31.4374	10.5650	5.9015	0.251

Excess molar volume and deviations of relative permittivity, viscosity, speed of sound and isentropic compressibility were fitted by a Redlich–Kister type equation [6]:

$$\Delta A = x_1 \cdot x_2 \sum_{j=0}^{k} a_j \cdot (2x_2 - 1)^j \tag{6}$$

where: $\Delta A = V^E$ ($cm^3\,mol^{-1}$) or $\Delta\varepsilon$ or $\Delta\ln\eta$ or Δu ($m\,s^{-1}$) or $\Delta\kappa$ ($T\,Pa^{-1}$).

The parameters a_j of equation (6) were evaluated by the least-squares method. The values of these parameters, with standard deviation σ, are summarized in table 2.

The standard deviation values were obtained from

$$\sigma = \left[\frac{\sum (X_{\text{exptl}} - X_{\text{calcd}})^2}{n - p}\right]^{1/2} \tag{7}$$

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.

Figure 1 shows that V^{E} values for ME + i-BA binary mixtures are negative over the whole mole fraction range, with a minimum lying always at $x_1 \approx 0.5$. The negative values of V^{E} are the results of contributions from several factors such as:

- the breakdown of self-associated structure of 2-methoxyethanol and isobutylamine;
- the intermolecular hydrogen bond formation in the 2-methoxyethanol and isobutylamine (formation of the stable intermolecular complex);
- specific interaction between unlike molecules in the studied binary mixtures.

Figure 2 shows that all $\Delta\varepsilon$ values are negative with a minimum lying always at $x_1 \approx 0.35$. As suggested by other authors [7,8], the study of this structural 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 plots of $\Delta\varepsilon$ *versus* x_1, could be taken as the true composition of these intermolecular complexes.

Figure 3 shows that all $\Delta\ln\eta$ values are positive with a maximum lying always at $x_1 \approx 0.55$. The positive values of $\Delta\ln\eta$ over the entire mole fraction range may be attributed mainly to the association through intermolecular hydrogen bonds between: $-NH_2$ group of the isobutylamine and hydrogen atom of the H–O– group of alkoxyethanol molecules and/or $-NH_2$ group of the isobutylamine and oxygen of the –O– groups of the alkoxyethanol molecules [9,10].

We have found $\Delta\kappa$ to be negative for all analysed systems over the entire composition range and it shows a minimum lying always at $x_1 \approx 0.50$. Negative values of $\Delta\kappa$ mean that the mixture is less compressible than the corresponding ideal mixture and it suggests that there may be strong intermolecular hydrogen bonding between the 2-methoxyethanol and isobutylamine molecules [11,12]. The behaviors of Δu are similar to that of $\Delta\kappa$ but with opposite sign (see figure 4). This is normal because the speed of sound is generally higher when the structure has high rigidity.

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

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