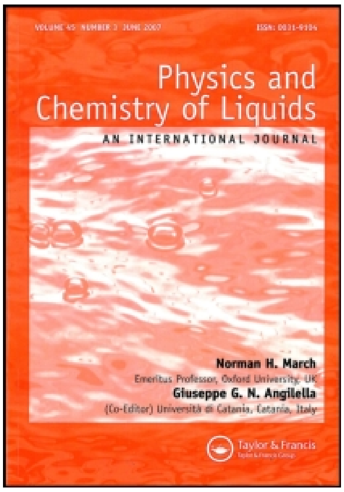

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Speed of sound of some aliphatic amines with 2-methoxyethanol mixtures at 298.15 K

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Speed of sound of some aliphatic amines with 2-methoxyethanol mixtures at 298.15 K

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The speed of sound of binary mixtures of 2-methoxyethanol with diethylamine, triethylamine, propylamine, dipropylamine, *sec*-butylamine and *tert*-butylamine has been measured as a function of composition at 298.15 K. From the experimental data, values of deviations in the speed of sound (Δu) and isentropic ($\Delta\kappa$) compressibility from ideality have been calculated. The results for Δu and $\Delta\kappa$ are discussed on the basis of intermolecular interactions between the components of the analysed mixtures.

Keywords: Speed of sound; 2-Methoxyethanol; Aliphatic amine

1. Introduction

In earlier papers [1–4] we reported the results of our investigations of the excess molar volumes for binary mixtures of 2-methoxyethanol (ME) with diethylamine (DEA), triethylamine (TEA), propylamine (PA), dipropylamine (DPA), *sec*-butylamine (*sec*-BA) and *tert*-butylamine (*tert*-BA) at different temperatures. These results suggested the relative importance of the hydrogen-bonding interactions between ME and aliphatic amine molecules. In continuation of these investigations, the present article reports the speed of sound, deviations in the speed of sound (Δu) and isentropic compressibility ($\Delta\kappa$) from ideality for binary mixtures containing ME with DEA, TEA, PA, DPA, *sec*-BA and *tert*-BA over the whole concentration range at 298.15 K.

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Table 1. Comparison of experimental speeds of sound of pure liquids with literature values at 298.15 K.

Solvent	u/m s^{-1} This work	Lit.
2-Methoxyethanol	1344.5	1332.0 [5]
Diethylamine	1119.3	1136.0 [6]
Triethylamine	1116.0	1123.0 [6]
Propylamine	1218.8	1224.0 [6]
Dipropylamine	1193.5	1198.0 [6]
sec-Butylamine	1180.2	–
tert-Butylamine	1068.4	–

2. Experimental section

2.1. *Materials*

2-Methoxyethanol, diethylamine, triethylamine, propylamine, dipropylamine, *sec*-butylamine and *tert*-butylamine (Merck, pro-analysis), containing less than 0.05% (w/w) of water, respectively (determined by Karl-Fischer method), were the same as these used in our earlier studies [1–4]. The mixtures were prepared by measuring 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 of 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 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 can be estimated as $\pm 0.5\,\mathrm{m\,s^{-1}}$. Values of speed of sound at 298.15 K were calculated by interpolation from the linear $u = f(T)$ function in the temperature range varying from 298.00 to 298.30 K.

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

3. Results and discussion

The experimental values of the speeds of sound at 298.15 K are summarised in table 2. From these experimental data and values of density (see our earlier papers [1–4]) the deviations in the speed of sound (Δu) and isentropic compressibility ($\Delta\kappa$) from a mole fraction average were calculated from the following equations [7,8]:

$$\Delta u = u - (x_1 \cdot u_1 + x_2 \cdot u_1) \tag{1}$$

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

Table 2. Speed of sound (u), deviations in the speed of sound, and isentropic compressibility ($\Delta\kappa$) of binary mixtures 2-methoxyethanol + aliphatic amine, at 298.15 K.

x_1	u/m s^{-1}	Δu/m s^{-1}	$\Delta\kappa/T$Pa^{-1}	x_1	u/m s^{-1}	Δu/m s^{-1}	$\Delta\kappa/T$Pa^{-1}
ME + DEA					ME + TEA		
0.0000	1119.3	0.0	0.0	0.0000	1116.0	0.0	0.0
0.0500	1132.6	2.0	−17.9	0.0500	1128.0	0.6	−9.3
0.1000	1145.6	3.8	−33.0	0.1020	1140.5	1.2	−17.7
0.1499	1158.3	5.2	−45.5	0.1502	1152.0	1.7	−24.3
0.2001	1170.8	6.4	−55.7	0.2001	1164.0	2.3	−30.2
0.2500	1183.4	7.8	−64.2	0.2504	1176.4	3.2	−35.7
0.3000	1196.0	9.1	−70.9	0.3011	1188.7	3.9	−39.9
0.3498	1208.3	10.2	−75.6	0.3501	1200.5	4.5	−42.9
0.4000	1220.3	10.9	−78.1	0.4005	1212.4	4.9	−44.8
0.4498	1231.9	11.3	−78.7	0.4508	1224.2	5.2	−45.7
0.4995	1243.1	11.3	−77.6	0.5002	1235.5	5.2	−45.4
0.5500	1254.0	10.8	−74.6	0.5503	1246.6	4.9	−44.0
0.5999	1264.4	10.0	−70.1	0.5998	1257.5	4.4	−41.7
0.6495	1274.4	8.8	−64.2	0.6499	1268.4	3.9	−38.7
0.7000	1284.5	7.6	−57.3	0.6995	1279.0	3.2	−34.8
0.7500	1294.3	6.1	−49.3	0.7498	1289.8	2.5	−30.3
0.8000	1304.1	4.6	−40.6	0.7992	1300.5	1.9	−25.3
0.8501	1314.0	3.3	−31.2	0.8504	1311.6	1.3	−19.6
0.8998	1324.0	2.1	−21.4	0.8992	1322.3	0.8	−13.7
0.9500	1334.3	1.1	−11.0	0.9510	1333.8	0.5	−7.0
1.0000	1344.5	0.0	0.0	1.0000	1344.5	0.0	0.0
ME + PA					ME + DPA		
0.0000	1218.8	0.0	0.0	0.0000	1193.5	0.0	0.0
0.0502	1227.6	2.5	−13.4	0.0501	1201.4	0.3	−3.4
0.1009	1237.1	5.6	−26.4	0.1000	1209.5	0.9	−6.9
0.1501	1245.7	8.0	−36.4	0.1502	1217.3	1.1	−9.3
0.2002	1254.3	10.3	−45.0	0.2001	1225.3	1.6	−11.7
0.2504	1262.6	12.3	−51.4	0.2508	1233.3	1.9	−13.4
0.3000	1270.5	14.0	−56.2	0.2999	1241.3	2.5	−15.5
0.3498	1278.1	15.3	−59.4	0.3502	1249.2	2.8	−16.6
0.3997	1285.2	16.2	−60.9	0.4000	1257.1	3.2	−17.5
0.4499	1291.8	16.4	−61.0	0.4500	1264.9	3.4	−18.1
0.4998	1298.0	16.4	−60.0	0.4999	1272.5	3.5	−18.0
0.5504	1303.7	15.7	−57.5	0.5507	1280.1	3.4	−17.5
0.6000	1308.8	14.6	−53.9	0.5982	1287.3	3.3	−16.9
0.6498	1313.6	13.1	−49.3	0.6502	1294.4	2.7	−15.1
0.6999	1317.9	11.1	−43.4	0.6999	1301.4	2.2	−13.3
0.7495	1322.1	9.1	−36.9	0.7489	1308.4	1.8	−11.4
0.8000	1326.1	6.7	−29.4	0.8015	1315.7	1.2	−9.0
0.8511	1330.3	4.5	−21.6	0.8496	1323.1	1.0	−7.3
0.8999	1334.5	2.6	−13.8	0.8997	1330.1	0.7	−4.8
0.9499	1339.1	0.9	−6.5	0.9497	1337.4	0.5	−2.5
1.0000	1344.5	0.0	0.0	1.0000	1344.5	0.0	0.0
ME + *sec*-BA					ME + *tert*-BA		
0.0000	1180.2	0.0	0.0	0.0000	1068.4	0.0	0.0
0.0505	1191.7	3.2	−14.1	0.0503	1086.3	4.0	−28.7
0.1005	1203.2	6.5	−26.6	0.1002	1103.9	7.8	−53.7
0.1496	1214.2	9.4	−37.1	0.1502	1121.0	11.1	−74.6
0.2008	1225.6	12.4	−46.4	0.2008	1137.9	14.1	−91.6
0.2492	1236.2	15.1	−53.8	0.2503	1154.6	17.1	−105.5
0.3002	1246.9	17.4	−59.5	0.3004	1170.6	19.2	−115.2
0.3495	1256.6	19.0	−63.2	0.3502	1186.2	21.1	−121.7
0.4009	1266.4	20.3	−65.5	0.4002	1201.2	22.3	−124.9
0.4491	1275.0	21.0	−66.1	0.4502	1215.7	23.0	−125.2
0.5001	1283.4	21.1	−65.1	0.5009	1229.8	23.1	−122.8
0.5489	1290.9	20.5	−62.7	0.5510	1243.1	22.6	−117.8

(*continued*)

Table 2. Continued.

x_1	$u/\mathrm{m\,s^{-1}}$	$\Delta u/\mathrm{m\,s^{-1}}$	$\Delta\kappa/T\,\mathrm{Pa^{-1}}$	x_1	$u/\mathrm{m\,s^{-1}}$	$\Delta u/\mathrm{m\,s^{-1}}$	$\Delta\kappa/T\,\mathrm{Pa^{-1}}$
ME + *sec*-BA				ME + *tert*-BA			
0.6001	1298.1	19.3	−58.8	0.6009	1255.8	21.5	−110.7
0.6489	1304.4	17.6	−53.8	0.6491	1267.5	19.9	−101.8
0.7009	1310.6	15.2	−47.5	0.7004	1279.7	17.9	−90.7
0.7456	1315.6	12.9	−41.3	0.7495	1290.6	15.3	−78.1
0.8006	1322.0	10.3	−33.4	0.8003	1301.9	12.5	−64.1
0.8496	1327.3	7.5	−25.5	0.8500	1312.8	9.7	−49.4
0.9005	1332.8	4.6	−17.0	0.9007	1323.6	6.5	−33.3
0.9489	1338.2	2.1	−8.5	0.9498	1333.7	3.1	−16.8
1.0000	1344.5	0.0	0.0	1.0000	1344.5	0.0	0.0

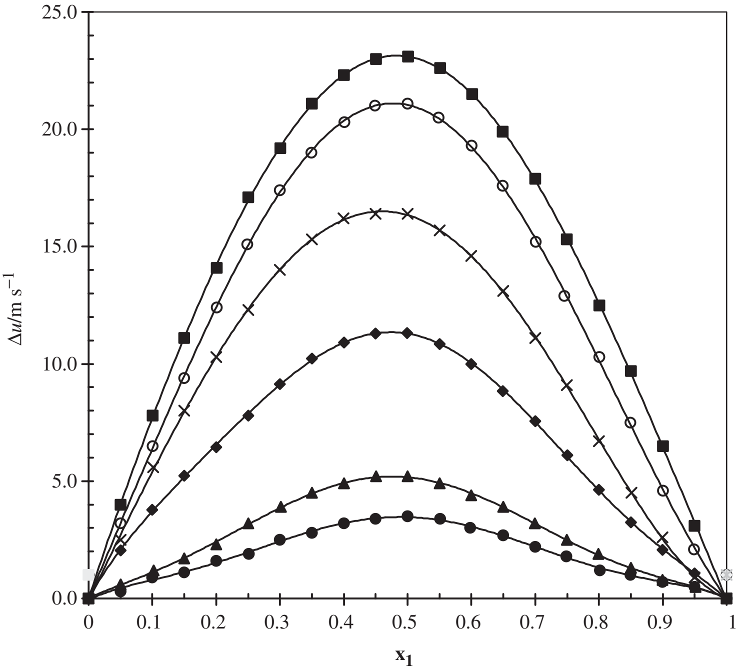

Figure 1. Plots of deviation speed of sound (Δu) against mole fraction ME for {(■) ME (1) + *tert*-BA (2)}, {(○) ME (1) + *sec*-BA (2)}, {(×) ME (1) + PA (2)}, {(◆) ME (1) + DEA (2)}, {(▲) ME (1) + TEA (2)} and {(●)ME (1) + DPA (2)} binary liquid mixtures, at $T = 298.15$ K.

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

The values of Δu and $\Delta\kappa$ of the binary mixtures are shown graphically in figures 1 and 2.

The deviations of speed of sound and isentropic compressibility were fitted by a Redlich–Kister type equation [9]:

$$\Delta u/\mathrm{m\,s^{-1}} \quad \text{or} \quad \Delta\kappa/T\ \mathrm{Pa^{-1}} = x_1 \cdot (1 - x_1) \sum_{j=0}^{k} a_j \cdot (2x_2 - 1)^j \qquad (3)$$

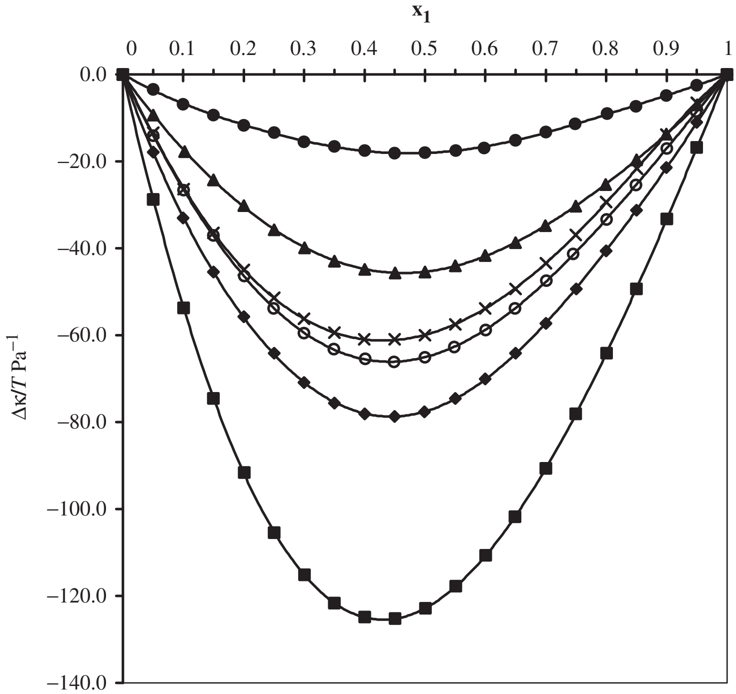

Figure 2. Plots of deviation isentropic compressibility ($\Delta\kappa$) against mole fraction ME for {(■) ME (1) + *tert*-BA (2)}, {(○) ME (1) + *sec*-BA (2)}, {(×) ME (1) + PA (2)}, {(◆) ME (1) + DEA (2)}, {(▲) ME (1) + TEA (2)} and {(●)ME (1) + DPA (2)} binary liquid mixtures, at $T = 298.15$ K.

The parameters a_j of equation (3) were evaluated by the least-squares method. The values of these parameters, at each studied temperature, with standard deviation σ, are summarised in table 3.

The standard deviation values were obtained from

$$\left[\frac{\sum (X_{\text{exptl}} - X_{\text{calcd}})^2}{n - p}\right]^{1/2} \tag{4}$$

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.

We have found $\Delta\kappa$ to be negative for all investigated systems over the entire composition range and to show minimum lying always near $x_1 \approx 0.50$, in the sequence:

$$\Delta\kappa_{\text{min}}^{\text{ME+}tert\text{-BA}} > \Delta\kappa_{\text{min}}^{\text{ME+DEA}} > \Delta\kappa > \Delta\kappa_{\text{min}}^{\text{ME+}sec\text{-BA}} > \Delta\kappa_{\text{min}}^{\text{ME+PA}} > \Delta\kappa_{\text{min}}^{\text{ME+TEA}} > \Delta\kappa_{\text{min}}^{\text{ME+DPA}}$$

Negative values of $\Delta\kappa$ mean that the mixture is less compressible than the corresponding ideal mixture, suggesting that there may be strong intermolecular hydrogen bonding between the ME and the aliphatic amine molecules [1–4,7,8,10,11]. These behaviours are qualitatively similar to that of excess molar volumes (V_m^E), which we reported in our earlier papers [1–4].

Table 3. Parameters a_j of equation (3), and standard deviations $\sigma(\Delta u)$ or $\sigma(\Delta\kappa)$ for 2-methoxyethanol + aliphatic amine binary mixtures.

	T [K]	a_0	a_1	a_2	a_3	
ME + DEA	298.15	44.2709	−8.4208	22.9115	−3.7500	$\sigma(\Delta u)/\mathrm{m\,s^{-1}} = 0.24$
ME + TEA	298.15	20.1188	−4.7381	−16.5314	4.7160	$\sigma(\Delta u)/\mathrm{m\,s^{-1}} = 0.15$
ME + PA	298.15	65.4215	−15.7914	−33.0276	−6.3688	$\sigma(\Delta u)/\mathrm{m\,s^{-1}} = 0.88$
ME + DPA	298.15	13.7352	−1.4117	−10.3647	1.9986	$\sigma(\Delta u)/\mathrm{m\,s^{-1}} = 0.15$
ME + *sec*-BA	298.15	83.8599	−10.9568	−35.6102	−1.3556	$\sigma(\Delta \mathrm{u})/\mathrm{m\,s^{-1}} = 0.09$
ME + *tert*-BA	298.15	92.1330	−8.5491	−21.8097	0.1172	$\sigma(\Delta u)/\mathrm{m\,s^{-1}} = 0.10$
ME + DEA	298.15	−309.0648	81.2958	17.4329	−2.5307	$\Delta\kappa/T\mathrm{Pa}^{-1} = 0.32$
ME + TEA	298.15	−180.9721	31.5351	15.7378	−8.4115	$\Delta\kappa/T\mathrm{Pa}^{-1} = 0.23$
ME + PA	298.15	−240.9907	71.2071	25.8787	23.4239	$\Delta\kappa/T\mathrm{Pa}^{-1} = 0.39$
ME + DPA	298.15	−71.6301	11.8952	15.0425	1.7441	$\Delta\kappa/T\mathrm{Pa}^{-1} = 0.23$
ME + *sec*-BA	298.15	−260.0777	70.2021	28.5156	−7.7365	$\Delta\kappa/T\mathrm{Pa}^{-1} = 0.16$
ME + *tert*-BA	298.15	−494.0429	149.2344	4.4768	−1.2384	$\Delta\kappa/T\mathrm{Pa}^{-1} = 0.18$

The behaviours of Δu are similar to that of $\Delta\kappa$ but with opposite sign (see figure 1 and table 2). This is normal because speed of sound is generally higher when the structure has high rigidity.

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