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Density and Speed of Sound of Binary Mixtures of *N*-Methyldiethanolamine and Triethanolamine with Ethanol

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In the present paper, density and speed of sound of binary systems formed by ethanol and two amines (*N*-methyldiethanolamine and triethanolamine) at several temperatures (15, 20, 25, 30, 35, and 40 °C) have been determined. The study of these mixtures has covered its complete composition range. Experimental values of these physical properties have been employed to calculate the isentropic compressibility value.

Introduction

Physical properties of pure amines and their mixtures with water are needed by different chemical engineering operations for the design of processes. The most important use of this kind of compound is for removal of sour gases from natural gas and petroleum streams. Other uses of these compounds are as surfactants, additives in detergents, and agriculture products.[1]

Alcohol solutions of triethanolamine (TEA) and *N*-methyldiethanolamine (MDEA) have been used recently as absorbent phases to remove carbon dioxide from gas streams.[2,3] Reaction between carbon dioxide and TEA has been established with a fast pseudo-first-order reaction. On the other hand, most researchers agree that MDEA does not react with carbon dioxide in nonaqueous solvents in the absence of water, and they state that the amount of carbon dioxide absorbed in a mixture of MDEA + ethanol was nearly the same as the amount which can be physically dissolved in the solution.[4]

The present work includes the measurement of density and speed of sound of MDEA (and TEA) + ethanol mixtures to obtain experimental data of these physical properties that could be useful in absorption/desorption studies to find an explanation for the mass transfer process and gas−liquid kinetics.

Experimental Section

Materials. *N*-Methyldiethanolamine (CAS Registry No. 105-59-9) and triethanolamine (CAS Registry No. 102-71-6) were supplied by Fluka and Sigma-Aldrich, respectively, with a purity of > 98 %. Ethanol has been supplied by Panreac Química (CAS No. 64-17-5) with a purity of > 99 %. All the mixtures were prepared by mass using an analytical balance (Kern 770) with a precision of $\pm 10^{-4}$ g. The maximum uncertainty of the sample's preparation in mole fraction was ± 0.002.

Methods. The density of pure components and a mixture of different solutes was measured with an Anton Paar DSA 5000 vibrating tube densimeter and sound analyzer, with an accuracy of $\pm 10^{-6}$ $\text{g}\cdot\text{cm}^{-3}$ in relation to density and ± 0.01 $\text{m}\cdot\text{s}^{-1}$ for the speed of sound. The uncertainty in the density and speed of sound measurements was $\pm 3\cdot10^{-5}$ $\text{g}\cdot\text{cm}^{-3}$ and ± 0.08 $\text{m}\cdot\text{s}^{-1}$, respectively.

The adiabatic compressibility, κ_s, was calculated from the speed of sound and density values using the Laplace equation

$$\kappa_s/\text{Pa}^{-1} = \frac{1}{(u/\text{m}\cdot\text{s}^{-1})^2\cdot(\rho/\text{kg}\cdot\text{m}^{-3})} \tag{1}$$

where u is the speed of sound and ρ is the density of the solution.

Results and Discussion

The values determined in the present paper for physical studies at different amine concentrations and temperatures in the range between (15 and 40) °C are listed in Tables 1 and 3 for the ethanol + *N*-methyldiethanolamine system and in Tables 2 and 4 for the ethanol + triethanolamine system. A comparison between the present work and bibliographic data of pure components at 25 °C has been carried out to confirm purity of liquid components and procedures for physical properties determinations. Bibliographic density/speed of sound data for ethanol, TEA, and MDEA are 0.78525[5]/1143,[6] 1.1215[7]/−, and 1.0369[7]/1568.3,[7] respectively. There was good agreement between the experimental values (see Tables 1 to 4) and the corresponding ones cited in the literature. Speed of sound values for pure TEA are not supplied in the literature.

The experimental density value for the two systems that have been studied indicates that an increase in temperature produces a continuous decreasing value of this property in a linear trend. With regard to the effect caused by a mixture composition, the presence of amines in the ethanol solutions produces an increase when amine concentration increases in the mixture. The behavior observed in the present paper is very common and similar to results obtained by other authors for water/amine systems.[8] In this figure, a comparison between experimental data obtained in the present work and the density determined in previous studies[9] for the same system at 40 °C has been plotted, and good agreement in this comparison has been observed.

In relation to speed of sound values, a similar trend has been observed in comparison with the previously described influence

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Table 1. Density, ρ, for MDEA (1) + Ethanol (2) from t = 15 °C to 40 °C

	ρ/(g·cm^{-3})					
x_1	t/°C = 15	t/°C = 20	t/°C = 25	t/°C = 30	t/°C = 35	t/°C = 40
0.0000	0.79360	0.78935	0.78506	0.78076	0.77600	0.77203
0.0049	0.79734	0.79308	0.78879	0.78448	0.77920	0.77541
0.0253	0.81093	0.80670	0.80207	0.79745	0.79251	0.78832
0.0524	0.82623	0.82203	0.81731	0.81297	0.80785	0.80395
0.1020	0.85532	0.85046	0.84579	0.84106	0.83599	0.83161
0.1629	0.88386	0.87900	0.87436	0.86983	0.86464	0.86034
0.2474	0.91648	0.91175	0.90718	0.90240	0.89720	0.89265
0.3713	0.95215	0.94750	0.94270	0.93824	0.93317	0.92865
0.4806	0.97720	0.97310	0.96828	0.96357	0.95875	0.95400
0.5506	0.99110	0.98670	0.98208	0.97752	0.97275	0.96798
0.7035	1.01370	1.00924	1.00504	1.00062	0.99608	0.99160
0.7916	1.02410	1.01988	1.01530	1.01124	1.00679	1.00249
0.8688	1.03269	1.02840	1.02420	1.01964	1.01581	1.01197
0.9415	1.03868	1.03496	1.03119	1.02742	1.02363	1.01982
1.0000	1.04432	1.04060	1.03683	1.03306	1.02926	1.02545

Table 2. Density, ρ, for TEA (1) + Ethanol (2) from t = 15 °C to 40 °C

	ρ/(g·cm^{-3})					
x_1	t/°C = 15	t/°C = 20	t/°C = 25	t/°C = 30	t/°C = 35	t/°C = 40
0.0000	0.79360	0.78935	0.78506	0.78076	0.77600	0.77203
0.0075	0.79961	0.79543	0.79134	0.78678	0.78253	0.77851
0.0184	0.80853	0.80451	0.80035	0.79627	0.79161	0.78772
0.0304	0.81800	0.81373	0.80959	0.80550	0.80105	0.79732
0.0622	0.84061	0.83637	0.83235	0.82841	0.82411	0.82047
0.1385	0.88941	0.88558	0.88174	0.87788	0.87356	0.86989
0.2275	0.93537	0.93177	0.92814	0.92444	0.92024	0.91668
0.3350	0.97949	0.97606	0.97267	0.96917	0.96520	0.96176
0.4675	1.02175	1.01853	1.01552	1.01227	1.00869	1.00544
0.6413	1.06429	1.06137	1.05861	1.05567	1.05255	1.04955
0.7790	1.09159	1.08873	1.08614	1.08338	1.08043	1.07753
0.8537	1.10443	1.10167	1.09923	1.09633	1.09346	1.09066
0.9328	1.11676	1.11401	1.11163	1.10888	1.10609	1.10323
1.0000	1.12619	1.12342	1.12099	1.11821	1.11538	1.11257

Table 3. Speed of Sound, u, for MDEA (1) + Ethanol (2) from t = 15 °C to 40 °C

	u/(m·s^{-1})					
x_1	t/°C = 15	t/°C = 20	t/°C = 25	t/°C = 30	t/°C = 35	t/°C = 40
0.0000	1179.0	1162.0	1144.9	1128.0	1111.1	1094.3
0.0049	1183.1	1166.0	1149.2	1132.3	1114.8	1098.8
0.0253	1201.7	1184.9	1168.0	1151.2	1134.5	1117.9
0.0524	1222.5	1205.9	1189.3	1172.7	1156.3	1139.8
0.1034	1260.9	1244.5	1228.1	1211.8	1195.6	1179.5
0.1629	1301.0	1286.0	1272.9	1257.3	1241.5	1225.8
0.2474	1353.0	1338.0	1325.0	1310.0	1293.0	1278.0
0.3713	1415.0	1399.7	1384.6	1369.4	1354.1	1339.0
0.4806	1460.0	1444.0	1429.2	1414.0	1398.8	1383.7
0.5530	1486.0	1470.0	1457.0	1439.0	1423.8	1408.7
0.7035	1536.0	1520.0	1500.0	1484.3	1468.9	1453.6
0.7916	1557.0	1542.0	1522.0	1505.6	1490.3	1475.1
0.8688	1573.2	1557.7	1538.0	1520.8	1506.2	1491.5
0.9415	1588.4	1572.9	1553.0	1535.0	1520.4	1506.1
1.0000	1598.8	1583.1	1564.0	1546.0	1531.0	1516.0

of mixture composition upon density value for the same systems. A continuous increment in this physical property is observed when the mixture composition increases in amine. Also, positive deviations were observed in the case of density and speed of sound values.

Excess volumes have been calculated using the expression shown in eq 2

$$V^{E} = \sum_{i=1}^{2} x_i M_i(\rho^{-1} - \rho_i^{-1}) \qquad (2)$$

where x is the molar fraction; M is the molecular weight; and

Table 4. Speed of Sound, u, for TEA (1) + Ethanol (2) from t = 15 °C to 40 °C

	u/(m·s^{-1})					
x_1	t/°C = 15	t/°C = 20	t/°C = 25	t/°C = 30	t/°C = 35	t/°C = 40
0.0000	1179.0	1162.0	1144.9	1128.0	1111.1	1094.3
0.0075	1185.2	1168.3	1151.4	1134.6	1117.9	1101.2
0.0184	1193.4	1176.9	1160.4	1143.9	1127.4	1111.1
0.0304	1202.1	1185.9	1170.0	1153.8	1137.7	1121.6
0.0622	1225.5	1210.0	1194.4	1178.9	1163.4	1148.0
0.1385	1277.0	1262.7	1248.6	1234.5	1220.4	1206.4
0.2275	1333.2	1320.0	1307.1	1294.3	1281.5	1268.8
0.3350	1397.0	1385.0	1373.1	1361.4	1349.9	1338.4
0.4675	1453.1	1442.5	1431.6	1420.9	1410.5	1400.1
0.6413	1528.0	1516.6	1505.9	1496.0	1486.6	1477.3
0.7790	1558.4	1546.8	1536.4	1526.6	1517.4	1508.5
0.8537	1597.9	1585.3	1574.3	1564.5	1555.6	1547.0
0.9328	1617.3	1604.6	1593.8	1584.2	1575.4	1567.1
1.0000	1640.5	1625.6	1614.5	1604.5	1595.5	1586.0

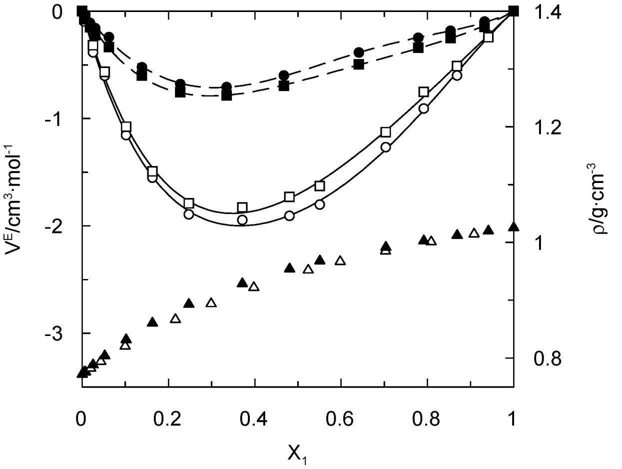

Figure 1. Excess molar volumes, V^E, for MDEA (1) + ethanol (2) systems (○, 20 °C; □, 40 °C) and the TEA (1) + ethanol (2) system (●, 20 °C; ■, 40 °C) and densities, ρ, for the MDEA (1) + ethanol (2) system at 40 °C: △, present work; ▲, Henni et al.[9]

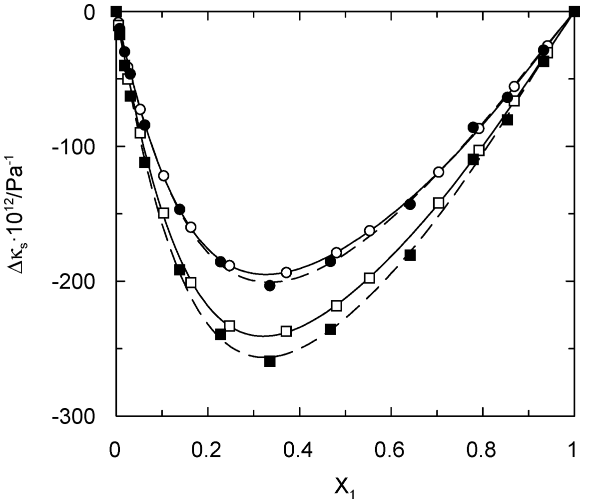

Figure 2. Isentropic compressibility deviations, $\Delta\kappa_S$, for the MDEA (1) + ethanol (2) system (○, 20 °C; □, 40 °C) and the TEA (1) + ethanol (2) system (●, 20 °C; ■, 40 °C).

ρ and ρ_i are the mixture density and the pure compound density, respectively.

Deviations from the isentropic compressibility coefficient have been calculated using eq 3.

$$\Delta Y = Y_m - (x_1 Y_1 + x_2 Y_2) \qquad (3)$$

An example of the calculated values corresponding to excess volumes for the experimental systems analyzed in the present work is shown in Figure 1. These data show, for both systems, negative deviations, similar to that previously observed for different amine systems[10] and also for the MDEA + ethanol system studied by other authors at 40 °C.[9]

Also, calculated deviations for isentropic compressibility values show negative values for all mixtures and temperatures. Similar deviations have been obtained for both systems, and when the temperature increases, the deviation also increases (see Figure 2).

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