Density, Speed of Sound, and Isentropic Compressibility of Triethanolamine (or *N*-Methyldiethanolamine) + Water + Ethanol Solutions from $t = (15 \text{ to } 50)$ °C

Alicia García-Abuín,[†] Diego Gómez-Díaz,[†] M. Dolores La Rubia,[‡] José M. Navaza,*,[†] and Rafael Pacheco[‡]

Department of Chemical Engineering, ETSE, University of Santiago de Compostela, Rúa Lope Gómez de Marzoa s/n, E-15706 Santiago de Compostela, Spain, and Department of Chemical, Environmental and Materials Engineering, EPS, University of Jaén, Paraje Las Lagunillas s/n, E-23071 Jaén, Spain

Density and speed of sound of ternary systems formed by water + ethanol + *N*-methyldiethanolamine or triethanolamine at a fixed volume ratio of ethanol to water of 50 % (ethanol mole fraction of 0.2336 corresponding to water + ethanol mixture) were determined at several temperatures (15, 20, 25, 30, 35, 40, 45, and 50 °C). Experimental values of these physical properties have been employed to calculate isentropic compressibility value.

Introduction

In the past decade, research studies about physical properties of aqueous solutions of amines or their mixtures have been developed to contribute valuable data to use in unit design or control of chemical processes.[1,2] One of the most important uses of this kind of compound is for removal of sour gases from natural gas and petroleum streams.[3,4] The main objective of these processes is related with gas streams cleaning and associated with minimization environmental pollution processes. Also, other uses of this kind of substance are as surfactants, additives in detergents, and agriculture products.

The use of nonaqueous solutions of alkanolamines has been commercially employed for different acid gases absorption because of their high solubility and capacity, their low corrosiveness, and their low energy consumption during regeneration.[5] Certain studies have shown that methanol could be used as a physical solvent for the removal of carbon dioxide from gas streams. Enhancement of the solubility of carbon dioxide in aqueous monoethanolamine (MEA) by the presence of methanol was observed at high partial pressures. The solubility was 25 % higher in a MEA + methanol mixture than in an aqueous MEA solution of equivalent concentration. Mixed solvents (chemical and physical) are expected to have a higher capacity for the acid gases over a wide range of partial pressures than the physical or chemical solvent alone.[6] Also, the use of ethanol as solvent in the CO_2 absorption processes could be of interest because different studies have shown that it improves absorption component.[5,6]

Present work includes the measurement of density and speed of sound for *N*-methyldiethanolamine (MDEA) + water + ethanol and triethanolamine (TEA) + water + ethanol systems.

* To whom correspondence should be addressed. E-mail: josemanuel.navaza@usc.es. Department of Chemical Engineering, University of Santiago de Compostela, Santiago de Compostela, E-15782 Galicia, Spain.
[†] University of Santiago de Compostela.
[‡] University of Jaén.

Table 1. Comparison of Experimental Results for Pure Components with Literature Data

t / °C	ρ / g·cm^{-3} experimental	ρ / g·cm^{-3} literature	t / °C	u / m·s^{-1} experimental	u / m·s^{-1} literature
		MDEA			
25	1.03683	1.03688[a] 1.03635[b] 1.038224[c]	25	1564.1	1568.3[a]
40	1.02545	1.02519[b] 1.026993[c] 1.0253[d]	35	1531.0	1537.8[a]
50	1.01778	1.01699[b] 1.019469[c] 1.0176[d]	45	1503.2	1507.0[a]
		TEA			
25	1.12099	1.1215[a]	25	1614.7	
40	1.11257	1.1156[e]	35	1595.4	
45	1.10978	1.1108[a]	45	1578.9	
		Ethanol			
25	0.78521	0.78510[f] 0.78522[g] 0.785085[h]	25	1144.2	1143.49[f] 1143.10[h]
35	0.77655	0.77643[f] 0.77551[i] 0.77726[j]	35	1110.5	1109.69[f] 1111.0[i]
45	0.76772	0.76762[f]	45	1076.9	1076.32[f]

[a] From ref 7. [b] From ref 8. [c] From ref 9. [d] From ref 1. [e] From ref 10. [f] From ref 11. [g] From ref 12. [h] From ref 13. [i] From ref 14. [j] From ref 15.

Experimental Section

Materials. MDEA (CAS Registry No. 105-59-9) and TEA (CAS Registry No. 102-71-6, TEA) were supplied by Fluka and Sigma-Aldrich, respectively, with a purity of > 98 %. Ethanol was supplied by Panreac Química (CAS No. 64-17-5) with a purity of > 99 %. The uncertainty of the samples' preparation in mole fraction was ± 0.0008.

Methods. The density of pure components and a mixture of different solutes were measured with an Anton Paar DSA 5000 vibrating tube densimeter and sound analyzer. The uncertainty in the density and speed of sound measurements was $\pm 2 \cdot 10^{-4}$ g·cm^{-3} and ± 0.3 m·s^{-1}, respectively.

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

10.1021/je900064e CCC: $40.75 © 2009 American Chemical Society
Published on Web 08/06/2009

$$\kappa_s = \frac{1}{u^2 \rho} \quad (1)$$

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

Results and Discussion

A comparison between the experimental results for density and speed of sound obtained in present work and the literature data for pure components at different temperatures has been included in Table 1, to confirm the purity of components and procedures for physical properties determination.

In the present study a mixture of ethanol + water (volume fraction of 50 %) has been employed to mix with different quantities of TEA and MDEA. The experimental values of water + ethanol density have been compared with the trend obtained in a previous study that analyzes the physical properties of water + ethanol blend.[16]

Tables 2 and 3 show the experimental results obtained for density and speed of sound for mixtures of TEA (and MDEA) + water + ethanol with a fixed relation of water and ethanol. These mixtures have covered the whole range of amines in mole fraction, and the measurements have been made for a wide range of temperatures t = (15 to 50) °C in steps of 5 °C.

The influence of mixture composition and the effect of temperature on density for these systems are shown in Figure

Table 2. Density, ρ, of TEA (1) (or MDEA) + Water (2) + Ethanol (3) Solutions from t = 15 to 50 °C

		ρ/g·cm^{-3}							
x_1	x_2	t/°C = 15	t/°C = 20	t/°C = 25	t/°C = 30	t/°C = 35	t/°C = 40	t/°C = 45	t/°C = 50
		TEA (1) + Water (2) + Ethanol (3) System							
0.0000	0.2336	0.93086	0.92708	0.92322	0.91931	0.91532	0.91127	0.90803	0.90432
0.0060	0.2322	0.93610	0.93311	0.92940	0.92533	0.92221	0.91852	0.9144	0.91041
0.0147	0.2302	0.94081	0.93788	0.93428	0.93128	0.92802	0.92373	0.91997	0.91567
0.0312	0.2263	0.95743	0.95391	0.95098	0.94741	0.94398	0.94027	0.93715	0.93383
0.1197	0.2056	1.01934	1.01581	1.01220	1.00859	1.00492	1.00118	0.99737	0.99352
0.2176	0.1827	1.05397	1.05059	1.04717	1.04369	1.04015	1.03657	1.03292	1.02914
0.3336	0.1557	1.07871	1.07491	1.07158	1.06867	1.06492	1.06213	1.05923	1.05644
0.4555	0.1272	1.09479	1.09179	1.08881	1.08571	1.08221	1.07914	1.07611	1.07259
0.5719	0.1000	1.10563	1.10272	1.09862	1.09462	1.09109	1.08863	1.08537	1.08272
0.6589	0.0797	1.11002	1.10788	1.10503	1.10182	1.09799	1.09419	1.09115	1.08806
0.8074	0.0450	1.11730	1.11450	1.11088	1.10729	1.10461	1.10181	1.09902	1.09696
0.8835	0.0272	1.12131	1.11852	1.11492	1.1120	1.10886	1.10580	1.10199	1.10058
1.0000	0.0000	1.12619	1.12342	1.12099	1.11821	1.11538	1.11257	1.10978	1.10693
		MDEA (1) + Water (2) + Ethanol (3) System							
0.0000	0.2336	0.93086	0.92708	0.92322	0.91931	0.91532	0.91127	0.90803	0.90432
0.0677	0.2178	0.96354	0.95971	0.95581	0.95188	0.94787	0.94380	0.93966	0.93597
0.1126	0.2073	0.97881	0.97500	0.97121	0.96713	0.96332	0.95926	0.95511	0.95132
0.2139	0.1836	1.00276	0.99864	0.99466	0.99029	0.98613	0.98203	0.97798	0.97404
0.2801	0.1682	1.01410	1.01012	1.00591	1.00191	0.99782	0.99359	0.98968	0.98590
0.4352	0.1319	1.02852	1.02467	1.02085	1.01696	1.01306	1.00911	1.00516	1.00141
0.5524	0.1045	1.03388	1.03011	1.02631	1.02248	1.01863	1.01474	1.01082	1.00746
0.6333	0.0857	1.03609	1.03234	1.02855	1.02474	1.02090	1.01730	1.01371	1.01042
0.7306	0.0629	1.03940	1.03567	1.03189	1.02810	1.02429	1.02045	1.01659	1.01343
0.8579	0.0332	1.04149	1.03781	1.03429	1.03029	1.02672	1.02299	1.01933	1.01587
0.9368	0.0148	1.04313	1.03948	1.03549	1.03171	1.02797	1.02419	1.02045	1.01701
1.0000	0.0000	1.04432	1.04060	1.03683	1.03306	1.02926	1.02545	1.02162	1.01778

Table 3. Speed of Sound, u, of TEA (1) (or MDEA) + Water (2) + Ethanol (3) Solutions from t = 15 to 50 °C

		u/m·s^{-1}							
x_1	x_2	t/°C = 15	t/°C = 20	t/°C = 25	t/°C = 30	t/°C = 35	t/°C = 40	t/°C = 45	t/°C = 50
		TEA (1) + Water (2) + Ethanol (3) System							
0.0000	0.2336	1546.7	1534.1	1521.1	1507.9	1494.5	1480.9	1467.0	1452.9
0.0060	0.2322	1554.1	1541.7	1527.5	1512.6	1499.2	1485.7	1471.8	1457.8
0.0147	0.2302	1560.8	1546.9	1534.5	1517.1	1503.9	1490.4	1476.4	1462.6
0.0312	0.2263	1572.7	1560.0	1546.0	1529.1	1516.2	1502.9	1489.3	1475.5
0.1197	0.2056	1615.1	1601.7	1590.4	1579.0	1567.3	1555.5	1543.0	1529.9
0.2176	0.1827	1628.9	1615.6	1605.8	1596.0	1586.2	1575.1	1563.8	1552.1
0.3336	0.1557	1633.2	1620.8	1611.5	1601.6	1593.9	1584.4	1574.4	1564.1
0.4555	0.1272	1635.2	1621.9	1612.0	1602.8	1594.7	1585.6	1576.3	1567.6
0.5719	0.1000	1636.5	1623.0	1612.5	1603.0	1594.9	1586.1	1577.6	1569.0
0.6589	0.0797	1637.1	1623.3	1612.8	1603.2	1595.0	1586.4	1577.9	1569.5
0.8074	0.0450	1638.5	1624.6	1613.1	1603.7	1595.2	1586.7	1578.1	1570.0
0.8835	0.0272	1639.8	1625.3	1613.5	1604.0	1595.3	1586.9	1578.6	1570.3
1.0000	0.0000	1641.3	1626.6	1614.7	1604.5	1595.4	1587.0	1578.9	1570.9
		MDEA (1) + Water (2) + Ethanol (3) System							
0.0000	0.2336	1546.7	1534.1	1521.1	1507.9	1494.5	1480.9	1467.0	1452.9
0.0677	0.2178	1583.9	1570.5	1557.0	1543.2	1529.1	1514.9	1500.3	1485.5
0.1126	0.2073	1607.3	1591.8	1577.6	1563.0	1548.4	1533.4	1518.3	1502.7
0.2139	0.1836	1628.7	1613.0	1597.4	1581.7	1566.4	1550.7	1534.4	1518.6
0.2801	0.1682	1634.8	1617.1	1601.4	1585.9	1570.3	1554.5	1538.5	1522.6
0.4352	0.1319	1640.0	1620.6	1604.6	1588.4	1574.2	1558.1	1542.0	1526.9
0.5524	0.1045	1629.2	1606.2	1590.7	1575.2	1559.8	1544.4	1528.9	1513.5
0.6333	0.0857	1620.0	1600.3	1584.8	1569.3	1553.8	1538.3	1522.8	1507.3
0.7306	0.0629	1613.1	1595.8	1579.3	1563.8	1548.5	1533.2	1518.2	1502.8
0.8579	0.0332	1606.4	1590.0	1571.5	1555.3	1541.1	1526.9	1510.8	1495.6
0.9368	0.0148	1601.7	1587.5	1566.7	1547.7	1534.5	1519.3	1504.2	1490.9
1.0000	0.0000	1598.8	1583.1	1564.1	1546.0	1531.0	1516.1	1503.2	1490.4

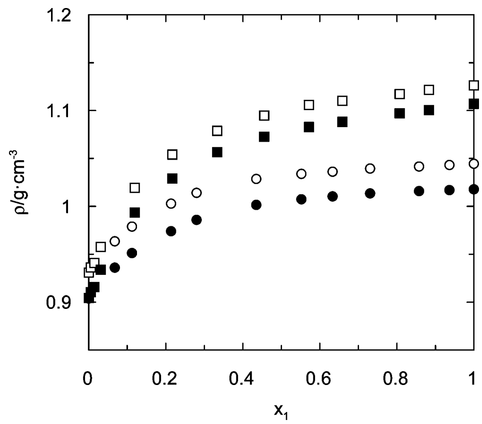

Figure 1. Influence of mixture composition on density. MDEA (1) + water (2) + ethanol (3): ○, 15 °C; ●, 50 °C. TEA + water (2) + ethanol (3): □, 15 °C; ■, 50 °C. Fixed water (2) to ethanol (3) mole ratio of 0.2336.

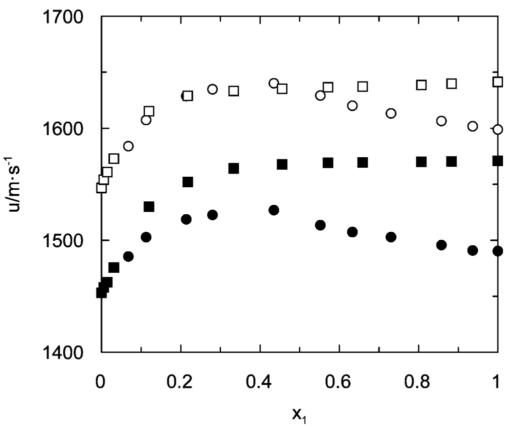

Figure 2. Influence of mixture composition on speed of sound. MDEA (1) + water (2) + ethanol (3): ○, 15 °C; ●, 50 °C. TEA (1) + water (2) + ethanol (3): □, 15 °C; ■, 50 °C. Fixed water (2) to ethanol (3) mole ratio of 0.2336.

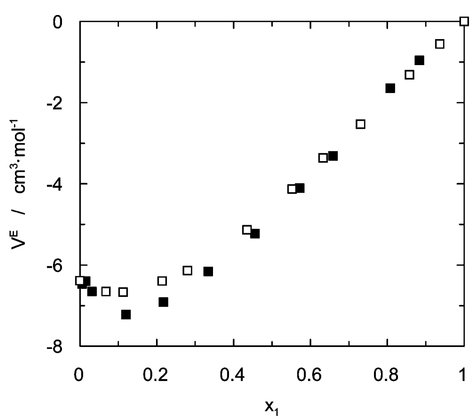

Figure 3. Influence of mixture composition on excess volume and isentropic compressibility deviation. ■, TEA (1) + water (2) + ethanol (3). □, MDEA (1) + water (2) + ethanol (3). T = 25 °C. Fixed water (2) to ethanol (3) mole ratio of 0.2336.

1. With regard to the influence of mixture composition on the value of density for both systems, an increase in amine composition in the liquid system indicates that the density shows a fast increase in its value, but this increase becomes more gradual as the mixture is enriched in amine. This behavior has been observed for all temperatures studied for this mixture. If the behavior observed is compared with the corresponding one for the system composed of these amines and ethanol,[17] the result is quite similar, although, in this case, the value of density for the "solvent" is higher because the ethanol is not pure since it is a mixture of ethanol and water.[17] With regard to the temperature effect, as usual, an increase in the value of the temperature produces a clear decrease of this physical property.

An example of the experimental results for the speed of sound is shown in Figure 2, observing that the behavior for each analyzed system has been different. Though for both systems, when liquid mixture is enriched in amine, an increase in the value of the speed of sound takes place, in the case of mixtures with TEA, a relatively constant value is reached for a mole fraction of around 0.3, and then, the value of speed of sound for the mixtures with higher amine compositions takes a value for this physical property quite similar to pure amine (TEA). However, in the case of MDEA mixtures, an increase in amine concentration also produces an increase in speed of sound values, but a maximum value is reached, also for a mole fraction of amine around 0.3. At higher mole fractions of MDEA, a slight decrease of the speed of sound value is observed until the value corresponds to pure amine. In the case of the speed of sound, a difference is observed with regard to the systems without water (only amine + ethanol),[17] because a continuous increase for the speed of sound was observed when the amine's concentration was increased in the mixture. In the present study using a mixture of water and ethanol, for the system with TEA, a constant value for the physical property is observed; however, in the case of the system with MDEA, a decrease for the mixtures with high compositions of amine is observed.

The obtained behavior for isentropic compressibility shows that a decrease in the value of this property is observed when amine concentration is increased in the mixture. An increase in temperature produces the opposite effect observed for density and speed of sound, and then it causes an increase in the value of isentropic compressibility.

Also, excess volume and isentropic compressibility deviations have been calculated using the common procedure described in previous studies.[17] Both properties and systems show negative values, and Figure 3 shows an example of the influence of composition upon excess volume behavior for both systems. Negative deviations indicate that interactions exist among unlike molecules. Large deviations were found that indicate strong hydrogen bonding interactions.

Literature Cited

(1) Zuñiga-Moreno, A.; Galicia-Luna, L. A.; Bernal-Garcia, J. M.; Iglesias-Silva, G. A. Densities, excess molar volumes, isothermal compressibilities, and isobaric thermal expansivities of the N-methyldiethanolamine (1) + water (2) system at temperatures between (313 and 363) K and pressures up to 20 MPa. *J. Chem. Eng. Data* **2007**, *52*, 1988–1995.

(2) Li, J.; Mundhwa, M.; Tontiwachwuthikul, P.; Henni, A. Volumetric properties, viscosities, and refractive indices for aqueous 2-(methylamino)ethanol solutions from (298.15 to 343.15) K. *J. Chem. Eng. Data* **2007**, *52*, 560–565.

(3) Gabrielsen, J.; Svendsen, H. F.; Michelsen, M. L.; Stenby, E. H.; Kontogeorgis, G. M. Experimental validation of a rate-based model for CO_2 capture using an AMP solution. *Chem. Eng. Sci.* **2007**, *62*, 2397–2413.

(4) Aboudheir, A.; Tontiwachwuthikul, P.; Idem, R. Rigorous model for predicting the behaviour of CO_2 absorption into AMP in packed-bed absorption columns. *Ind. Eng. Chem. Res.* **2006**, *45*, 2553–2557.

(5) Park, S.-W.; Choi, B.-S.; Lee, J.-W. Chemical absorption of carbon dioxide with triethanolamine in non-aqueous solutions. *Korean J. Chem. Eng.* **2006**, *23*, 138–143.

(6) Henni, A.; Mather, A. E. Solubility of carbon dioxide in methyldiethanolamine + methanol + water. *J. Chem. Eng. Data* **1995**, *40*, 493–495.

(7) Hawrylak, B.; Burke, S. E.; Palepu, R. Partial molar and excess volumes and adiabatic compressibilities of binary mixtures of ethanolamines with water. *J. Solution Chem.* **2000**, *29*, 575–594.
(8) Henni, A.; Maham, Y.; Tontiwachwuthikul, P.; Chakma, A.; Mather, A. E. Densities and viscosities for binary mixtures of N-methyldiethanolamine + triethylene glycol monomethyl ether from 25 to 70 °C and N-methyldiethanolamine + ethanol mixtures at 40 °C. *J. Chem. Eng. Data* **2000**, *45*, 247–253.
(9) Muhammad, A.; Mutalib, M. I. A.; Murugesan, T.; Shafeeq, A. Density and excess properties of aqueous N-methyldiethanolamine solutions from (298.15 to 338.15) K. *J. Chem. Eng. Data* **2008**, *53*, 2217–2221.
(10) DiGuillo, R. M.; Lee, R.-J.; Schaeffer, S. T.; Brasher, L. L.; Teja, A. S. Densities and viscosities of the ethanolamines. *J. Chem. Eng. Data* **1992**, *37*, 239–242.
(11) Zafarani-Moattar, M. T.; Majdan-Cegincara, R. Density, speed of sound, and viscosity of binary mixtures of poly(propyleneglycol) 400 + ethanol and + 2-propanol at different temperatures. *J. Chem. Eng. Data* **2008**, *53*, 2211–2216.
(12) Arce, A.; Rodil, E.; Soto, A. Volumetric and viscosity study for the mixtures of 2-ethoxy-2-methylpropane, ethanol, and 1-ethyl-3-methylimidazolium ethyl sulfate ionic liquid. *J. Chem. Eng. Data* **2006**, *51*, 1453–1457.
(13) Zafarani-Moattar, M. T.; Sadeghi, R.; Sarmad, S. Measurement and modelling of densities and sound velocities of the systems {poly (propylene glycol) + methanol, + ethanol, + 1-propanol, + 2-propanol and + 1-butanol} at T) 298.15 K. *J. Chem. Thermodyn.* **2006**, *38*, 257–263.
(14) Kadam, U. B.; Hiray, A. P.; Sawant, A. B.; Hasan, M. Densities, viscosities, and ultrasonic velocity studies of binary mixtures of trichloromethane with methanol, ethanol, propanol-1-ol, and butanol-1-ol at T) (298.15 and 308.15) K. *J. Chem. Thermodyn.* **2006**, *38*, 1675–1683.
(15) Mutalik, V.; Manjeshwar, L.; Sairam, M.; Aminabhavi, T. M. Thermodynamic interactions in binary mixtures of anisole with ethanol, propanol-1-ol, propanol-2-ol, butanol-1-ol, pentanol-1-ol, and 3-methylbutan-1-ol at T) (298.15, 308.15, and 318.15) K. *J. Chem. Thermodyn.* **2006**, *38*, 1620–1628.
(16) González, B.; Calvar, N.; Gómez, E.; Domínguez, A. Density, dynamic viscosity, and derived properties of binary mixtures of methanol or ethanol with water, ethyl acetate, and methyl acetate at T = (293.15, 298.15, and 303.15) K. *J. Chem. Thermodyn.* **2007**, *39*, 1578–1588.
(17) Álvarez, E.; Gómez-Díaz, D.; La Rubia, M. D.; Navaza, J. M.; Pacheco, R.; Sánchez, S. Density and speed of sound of binary mixtures of N-methyldiethanolamine and triethanolamine with ethanol. *J. Chem. Eng. Data* **2007**, *52*, 2059–2061.

Received for review February 10, 2009. Accepted July 23, 2009.

JE900064E