Speed of Sound and Isentropic Compressibility of Aqueous Solutions of Pyrrolidine and Piperidine

Diego Gómez-Díaz and José M. Navaza*

Department of Chemical Engineering, ETSE, University of Santiago de Compostela, Rúa Lope Gómez de Marzoa s/n E-15782, Santiago de Compostela, Spain

In the present paper, speed of sound and isentropic compressibility of aqueous solutions of two amines, pyrrolidine (C_4H_9N) and piperidine ($C_5H_{11}N$), at several temperatures (293, 303, 313, and 323 K) have been determined. The study of these mixtures has covered its complete composition range. Speed of sound shows a maximum value when the presence of amines increases in the mixture. A Redlich−Kister type equation was employed to fit the excess properties.

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 compounds is for removal of sour gases from natural gas and petroleum streams. The main objective of these processes is to minimize the environmental pollution and, specifically, the greenhouse effect. In particular, aqueous solutions of different amines could be used to determine interfacial areas in gas−liquid contactors by a chemical method. Other uses of these compounds are as surfactants, additives in detergents, and agriculture products.[1]

Different physical properties (density, viscosity, speed of sound, surface tension, thermal conductivity, etc.) of pure amines and different mixtures with water have been studied previously.[2,3] In previous papers, other authors have analyzed different amine−water systems in relation to the important physical properties with influence in several industrial operations.[4,5]

Aqueous solutions of pyrrolidine have been employed as liquid absorbent to remove carbon dioxide.[6] In relation with the amines used in the present paper, Minevich and Marcus[7] have been developed previous studies related with the density behavior of aqueous solutions of pyrrolidine at 298 and 323 K. Teitel'baum et al.[8] have also developed experimental studies in the water + piperidine system, determining density, viscosity, surface tension, and refractive index of this binary mixture at 273, 298, 323, and 358 K. Our research group developed a study that increases the experimental data for these systems for density and viscosity.[9,10]

The present paper includes physical characterization in relation to speed of sound, isentropic compressibility, and corresponding excess properties of aqueous solutions of piperidine and pyrrolidine over the entire range of composition. Physical properties have been measured in the range of temperatures between 293 and 323 K in order to cover the temperature range found in industrial applications.

Experimental Section

Materials. Pyrrolidine (CAS Registry No. 123-75-1) and piperidine (CAS Registry No. 110-89-4) were supplied by Fluka and Riedel-de Haën, respectively, with a purity of > 99 % and > 99.5 %. Bidistilled water was used to prepare the mixtures of water and amine. All the mixtures were prepared by mass using an analytical balance (Kern 770) with a precision of ± 10^{-4} g. The maximum uncertainty of the samples preparation in mole fraction was ± 0.002.

Table 1. Speeds of Sound, *u*, for Water (1) + Pyrrolidine (2) from 293 K to 323 K.

	u/m·s^{-1}			
x_2	T = 293 K	T = 303 K	T = 313 K	T = 323 K
1.000	1389.4	1348.0	1305.8	1263.0
0.868	1416.6	1375.5	1333.8	1291.7
0.686	1467.5	1426.8	1385.6	1344.0
0.567	1500.3	1458.9	1422.2	1377.7
0.483	1528.8	1489.9	1450.5	1410.5
0.396	1556.7	1519.5	1481.6	1443.0
0.304	1589.8	1555.3	1520.0	1483.9
0.208	1626.3	1596.4	1565.5	1533.5
0.116	1654.8	1631.8	1608.0	1583.2
0.068	1650.5	1635.1	1619.3	1602.3
0.022	1557.9	1569.8	1576.6	1578.7
0.010	1517.1	1537.1	1551.1	1559.7
0.006	1501.6	1525.2	1541.5	1552.2
0.000	1482.6	1509.2	1529.0	1542.6

Methods. Speed of sound of the pure liquids and its mixtures were measured with an Anton Paar DSA 5000 sound analyzer with a precision of ± 0.1 m·s^{-1}. The apparatus allow varying the temperature in the range used in the present study. The uncertainty of measurements was ± 0.6 m·s^{-1}. The measurements were carried out at atmospheric pressure.

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

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

where u is the speed of sound and ρ is the density of the solution. The density values have been obtained from literature for the aqueous solutions of the amines employed in the present study.[9]

Results and Discussion

The values determined and calculated in the present paper at different amine concentrations and temperatures in the range between 293 and 323 K are listed in Tables 1 and 3 for the

* Corresponding author e-mail: eqnavaza@usc.es.

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Table 2. Speeds of Sound, *u*, for Water (1) + Piperidine (2) from 293 K to 323 K

	u/m·s^{-1}			
x_2	T = 293 K	T = 303 K	T = 313 K	T = 323 K
1.000	1384.4	1342.3	1299.9	1257.4
0.846	1406.2	1365.1	1323.6	1282.0
0.646	1445.3	1405.2	1364.8	1324.2
0.523	1477.0	1438.0	1398.6	1358.9
0.439	1499.8	1461.1	1424.0	1384.9
0.354	1525.1	1489.1	1452.5	1415.4
0.267	1550.2	1517.2	1483.5	1449.0
0.180	1575.4	1547.9	1519.2	1489.3
0.099	1593.6	1576.5	1557.5	1536.6
0.057	1596.3	1587.1	1576.0	1562.7
0.028	1590.1	1588.3	1584.5	1578.3
0.011	1531.1	1548.7	1560.4	1566.8
0.006	1506.5	1528.7	1544.8	1555.1
0.000	1482.5	1509.2	1529.0	1542.6

Table 3. Isentropic Compressibilities, κ_s, for Water (1) + Pyrrolidine (2) from 293 K to 323 K

	κ_s·10^{12}/Pa^{-1}			
x_2	T = 293 K	T = 303 K	T = 313 K	T = 323 K
1.000	602.4	647.4	697.9	751.7
0.868	571.2	612.6	659.0	708.1
0.686	519.9	555.9	596.1	640.9
0.567	490.4	524.0	558.1	599.8
0.483	466.5	496.3	529.3	566.0
0.396	444.3	471.1	500.6	533.5
0.304	419.3	442.4	467.8	495.9
0.208	392.9	411.4	431.9	454.5
0.116	372.2	385.8	400.6	416.8
0.068	371.0	380.3	390.3	401.5
0.022	414.3	409.4	407.6	408.5
0.010	436.0	426.0	419.9	417.2
0.006	444.7	432.2	424.6	420.7
0.000	455.7	440.9	431.1	425.3

Table 4. Isentropic Compressibilities, κ_s, for Water (1) + Piperidine (2) from 293 K to 323 K

	κ_s·10^{12}/Pa^{-1}			
x_2	T = 293 K	T = 303 K	T = 313 K	T = 323 K
1.000	968.0	1020.2	1077.1	1139.0
0.846	928.6	977.3	1030.4	1088.1
0.646	867.6	911.3	958.7	1010.3
0.523	823.8	863.7	907.0	954.0
0.439	792.0	830.1	868.8	913.6
0.354	761.6	795.3	831.8	871.4
0.267	729.7	759.5	791.7	826.6
0.180	694.9	719.4	746.0	774.9
0.099	660.6	677.5	696.1	716.7
0.057	644.9	656.6	669.8	684.9
0.028	638.4	645.1	653.5	663.8
0.011	658.5	654.9	655.1	658.6
0.006	667.6	661.5	659.5	661.1
0.000	676.9	668.3	664.3	664.0

water + pyrrolidine system and in Tables 2 and 4 for the water + piperidine system.

Figure 1 shows the behavior observed for speed of sound when the effect produced for the water−amine mixtures composition was analyzed. In Figure 1, it is possible to observe that, at low amine (piperidine) concentration in the mixture, the speed of sound increases continuously when the amine presence increases, but when amine concentration reaches values close to 0.05 of amine mole fraction, the value of speed of sound reaches a maximum. When this maximum has been reached, this property decreases continuously when the amine concentration increases in the mixture. The commented behavior has been observed for all temperatures analyzed and for all the systems included in the present paper. Similar behaviors were observed for other systems.[11]

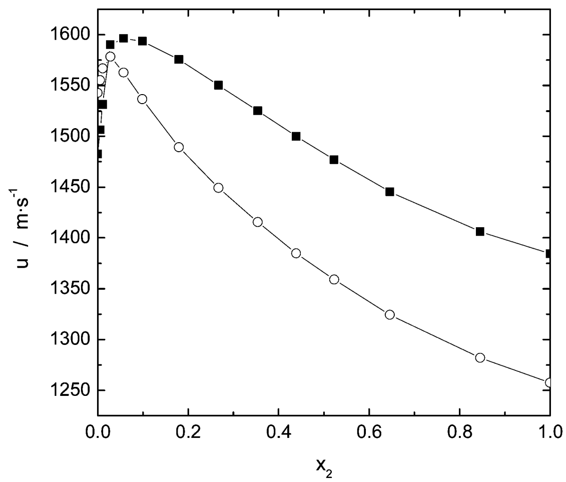

Figure 1. Effect of mixture composition on speed of sound u of water (1) + piperidine (2): ■, 293 K; ○, 323 K.

Table 5. Fit Parameters Corresponding to Equation 3 for the Water (1) + Piperidine (2) System

	$\Delta\kappa_s$·10^{12}/Pa^{-1}			
parameter	T = 293 K	T = 303 K	T = 313 K	T = 323 K
q_1	−2906.4	−2183.7	−1623.0	−1164.2
q_2	11864.5	9491.5	7792.6	6445.9
q_3	−16545.4	−13562.7	−11579.9	−9982.6
q_4	7797.5	6482.6	5668.8	4984.1

In relation to the effect of temperature upon this physical property, different behaviors were found at different mixture composition ranges. In Figure 1, at very low amine composition in the mixture, the speed of sound increases its value when the temperature increases too. When the mixture enriches in amine, the value of speed of sound at different temperatures reaches similar values (near to the maximum previously commented). The maximum is surpassed when the amine composition increases in the binary mixture and the value of speed of sound takes low values at high temperatures while at low values of temperature increases the value for this physical property. Then it exists as a water/amine composition in which at different temperatures, in the composition range studied in the present paper, the speed of sound takes the same value, as can be seen in Figure 1. Similar behavior was found in other studies such as the effect of phase-transfer catalysts upon the percolation temperature of microemulsions.[12] These studies were carried out for our research group, and the mixture composition that cancelled the effect of one variable upon the value of some physical property was deternubed, This composition is called compensating composition.

The isentropic compressibility (κ_s) of mixtures employed in the present work, were defined by

$$\Delta Y = Y_m - (x_1 Y_1 + x_2 Y_2) \tag{2}$$

The deviation values were fitted using a well-know Redlich−Kister type equation[13] (eq 3) used in a great number of studies of liquid mixtures. The results obtained for fitting parameters are shown in Tables 5 and 6, and Figure 2 shows the fit of the Redlich−Kister equation to the calculated values of isentropic compressibility from the speed of sound experimental values:

$$\Delta\kappa_s/\text{Pa}^{-1} = x_1 x_2 \sum_{j=1}^{4} (q_j/\text{Pa}^{-1}) x_2^{(j-1)/2} \tag{3}$$

For both the systems, the values of $\Delta\kappa_s$ are negative over the

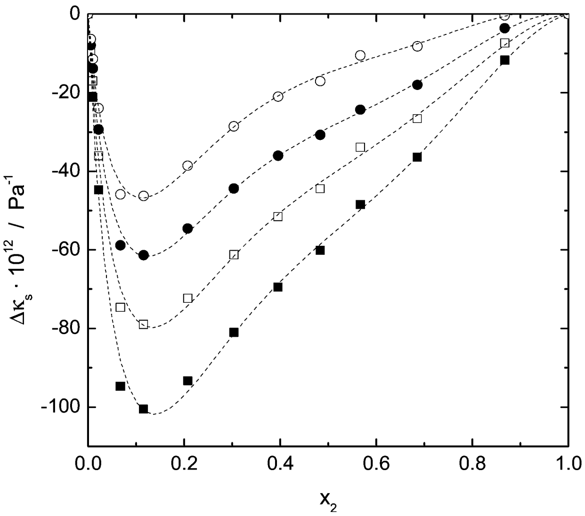

Figure 2. Isentropic compressibility deviations $\Delta\kappa_s$ for water (1) + pyrrolidine (2) system: ○, 323 K; ●, 313 K; □, 303 K; ■, 293 K.

Table 6. Fit Parameters Corresponding to Equation 3 for the Water (1) + Pyrrolidine (2) System

	$\Delta\kappa_s \cdot 10^{12}/Pa^{-1}$			
parameter	T = 293 K	T = 303 K	T = 313 K	T = 323 K
q_1	−3743.3	−3003.1	−2478.0	−2003.0
q_2	12556.5	10152.9	8637.6	7103.8
q_3	−1562.3	−12357.9	−10745.3	−8796.4
q_4	6416.1	5195.5	4602.0	3728.7

entire composition range and at all the temperatures studied. This indicates that the mixtures are more compressible than the corresponding ideal mixture. Due to these interactions, the ultrasonic velocity increases, and the compressibility of these solutions decreases until the minima are reached. Then these parameters follow the reverse trend. From these considerations, it is clear that there is a strong association the systems studied in the present work.

Literature Cited

(1) Astarita, G.; Savage, D. W.; Bisio, A. *Gas Treating with Chemical Solvents*; Wiley: New York, 1983.

(2) Mahan, Y.; Lebrette, L.; Mather, A. E. Viscosities and excess properties of aqueous solutions of mono- and diethylethanolamines at temperatures between 198.15 and 353.15 K. *J. Chem. Eng. Data* **2002**, *47*, 550−553.

(3) Yoon, S. J.; Lee, H.-S.; Lee, H.; Baek, J.-I.; Yoon, J.-H.; Eum, H.-M. Densities, viscosities, and surface tensions of aqueous 2-amino-2-ethyl-1,3-propanediol solutions. *J. Chem. Eng. Data* **2002**, *47*, 30−32.

(4) Henni, A.; Hromek, J. J.; Tontiwachwuthikul, P.; Chakma, A. Volumetric properties and viscosities for aqueous diisopropanolamine solutions from 25 °C to 70 °C. *J. Chem. Eng. Data* **2003**, *48*, 1062−1067.

(5) Hsu, C.-H.; Li, M.-H. Viscosities of aqueous blended amines. *J. Chem. Eng. Data* **1997**, *42*, 714−720.

(6) Bonenfant, D.; Mimeault, M.; Hausler, R. Determination of the structural features of distinct amines important for the absorption of CO_2 and regeneration in aqueous solution. *Ind. Eng. Chem. Res*. **2003**, *42*, 3179−3184.

(7) Minevich, A.; Marcus, Y. Densities and excess and partial molar volumes of aqueous pyrrolidine at 25 and 50 °C and aqueous morpholine at 25 and 60 °C *J. Chem. Eng. Data* **2003**, *48*, 208−210.

(8) Teitel′baum, B. Ya.; Trifonov, N. A.; Khachatur'yan, V. R. Physico-chemical analysis of the system water−piperidine. *Zh. Fiz. Khim.* **1947**, *21*, 503−508.

(9) Álvarez, E.; Gómez-Díaz, D.; La Rubia, D.; Navaza, J. M.·Effect of composition and temperature upon densities, viscosities and excess properties of aqueous solutions of pyrrolidine and piperidine. *J. Chem. Eng. Data* **2005**, *50*, 1829−1832.

(10) Gómez-Díaz, D.; Navaza, J. M. Surface behavior of aqueous solutions of pyrrolidine and piperidine. *J. Chem. Eng. Data* **2004**, *49*, 1406−1409.

(11) Pitchai, J. V.; Dilip, K. H. Excess molar volumes, viscosity deviations, and isentropic compressibility changes in binary mixtures of *N*-methylacetamide + 2-methoxyethanol and *N*-methylacetamide + water at (308.15, 313.15, and 318.15) K. *J. Chem. Eng. Data* **2002**, *47*, 79−82.

(12) Dasilva-Carvalhal, J.; García-Río, L.; Gómez-Díaz, D.; Mejuto, J. C.; Navaza, J. M. Conductivity of sodium bis(2-ethylhexyl)sulfosuccinate + isooctane + water microemulsions containing phase-transfer catalysts. 3. *J. Chem. Eng. Data* **2005**, *50* 529−535.

(13) Redlich, O.; Kister, A. T. Algebraic representation of thermodinamics properties and the classification of the solutions. *Ind. Eng. Chem*. **1948**, *40*, 345−348.

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