Densities, Viscosities, Surface Tensions, and Speeds of Sound of Aqueous Solutions of Piperidine + Pyrrolidine + Water

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In the present paper, density, viscosity, speeds of sound, and surface tension have been determined for piperidine + pyrrolidine + water ternary aqueous solutions at 20 °C. The experimental results have been correlated with a Redlich−Kister type equation.

Introduction

Mixtures of amines with water have been used in processes related to natural gas, ammonia synthesis, etc., to remove acid gases such as carbon dioxide by means of a chemical reaction between acid gases and the amines.[1,2] Different amines have been used commonly to remove selectively acid gases present in the mixtures, that is, monoethalamine (MEA), *N*-methyldiethanolamine (MDEA), or triethanolamine (TEA),[3] and other amines have been studied in laboratories to analyze the properties for their use in this process.

The use of aqueous amine solutions as an absorbent involves knowledge of the physicochemical properties of these systems, thatis, gas−liquid diffusivity,[4] because they are used to calculate essential parameters when absorption processes are analyzed. Several studies[4] have been aimed at analyzing the effect of physicochemical properties upon processes such as carbon dioxide absorption in aqueous amine solutions.

Different new amines have been employed to remove acid gases, and aqueous solutions of pyrrolidine have also been employed as liquid absorbent to remove carbon dioxide.[5] Related to the amines used in the present paper, Minevich and Marcus[6] have studied the volumetric properties of aqueous pyrrolidine solutions at (25 and 50) °C. Teitel'baum et al.[7] have made studies on the water + piperidine system, determining the density, viscosity, surface tension, and refractive index of this binary mixture at (0, 25, 50, and 75) °C. Several physicochemical properties corresponding to aqueous binary mixtures of these amines have been determined by our research team.[8]

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 purities of > 99 % and > 99.5 %. Double-distilled water was used to prepare the mixtures of water and amine. All of the mixtures were prepared by mass using an analytical balance (Kern 770) with a precision of $\pm 10^{-4}$ g. The uncertainty of the sample preparation in mole fraction was $\pm 4 \cdot 10^{-4}$.

Methods. Density ρ and speed of sound u of the pure liquids and their mixtures were measured with an Anton Paar DSA 5000 vibration tube densimeter and sound analyzer, respectively, with a precision of $\pm 10^{-6}$ g·cm^{-3} for density and $\pm$ 0.1 m·s^{-1} for speed of sound. The apparatus allows the temperature to be varied in the range used in the present study. The uncertainty in the density measurement was $\pm 5 \cdot 10^{-5}$ g·cm^{-3}, whereas that for speed of sound was $\pm$ 0.6 m·s^{-1}.

The kinematic viscosity ν was determined from the efflux time of the liquid meniscus through a capillary supplied by Schott [cap no. 0c, (0.46 $\pm$ 0.01) mm of internal diameter, K = 0.003201 mm^2·s^{-2}] with an uncertainty of $\pm 5 \cdot 10^{-4}$ mm^2·s^{-1} using eq 1

$$\nu = K \cdot (t - \theta) \tag{1}$$

where t is the efflux time, K is the characteristic constant of the capillary viscosimeter, and θ is a correction value to correct the final effects. The glass capillary was connected to a Schott-Geräte AVS 350 viscometer unit. An electronic stopwatch with

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Table 1. Density ρ, Viscosity η, and Surface Tension σ of Pure Piperidine and Pyrrolidine

	ρ/g·cm^{-3} at t = 20 °C	η/mPa·s at t = 20 °C	σ/mN·m^{-1} at t = 25 °C
piperidine	0.86381[a]	1.5506[a]	29.56[a]
	0.8606[b]	1.559[c]	29.48[e]
	0.862[c]		
pyrrolidine	0.85987[a]	0.8207[a]	29.75[a]
	0.8586[b]	0.799[c]	29.65[e]
	0.864[c]		
	0.856[d]		

[a] Present paper. [b] *CRC Handbook of Chemistry and Physics*.[9] [c] *Chemical Properties Handbook Physical, Thermodynamic, Environmental, Transport, Safety and Health Related Properties for Organic and Inorganic Chemicals*.[10] [d] *Handbook of Tables for Organic Compounds Identification*.[11] [e] Jasper.[12]

Table 2. Density, Viscosity, Speed of Sound, and Surface Tension of Binary Mixtures of Piperidine (1) + Pyrrolidine (2)

x_1	ρ/g·cm^{-3}	η/mPa·s	u/m·s^{-1}	σ/mN·m^{-1}
1.0000	0.85987	0.8207	1389.4	30.27
0.8273	0.86160	0.9124	1391.5	30.42
0.7053	0.86189	0.9752	1390.8	30.47
0.6423	0.86219	1.0381	1390.1	30.51
0.4960	0.86279	1.2010	1388.2	30.56
0.2304	0.86340	1.3642	1386.3	30.61
0.1043	0.86361	1.4573	1385.4	30.36
0.0000	0.86381	1.5506	1384.4	30.11

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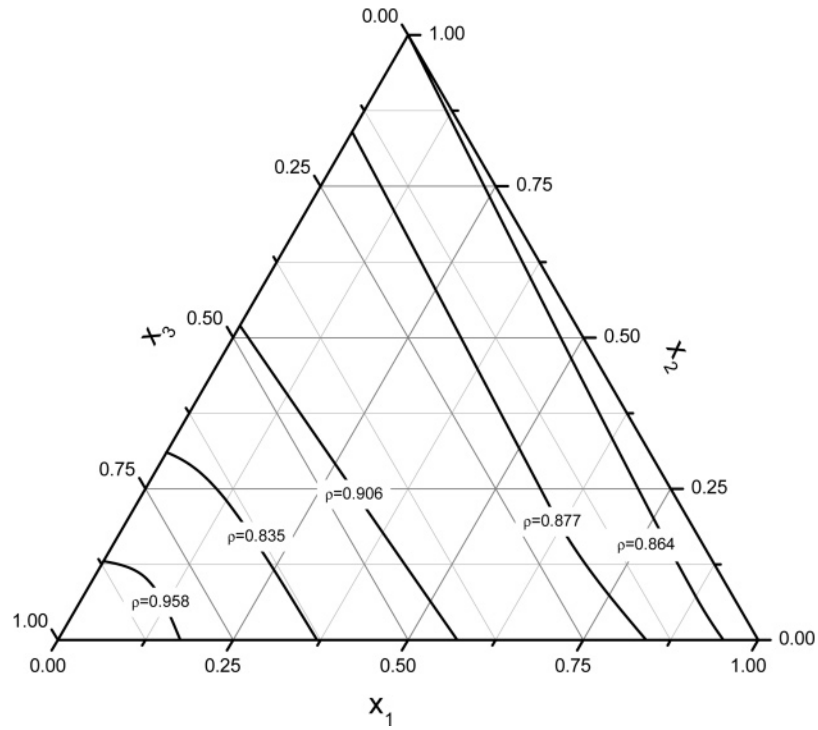

Figure 1. Influence of mixture composition on density for pyrrolidine (1) + piperidine (2) + water (3) system.

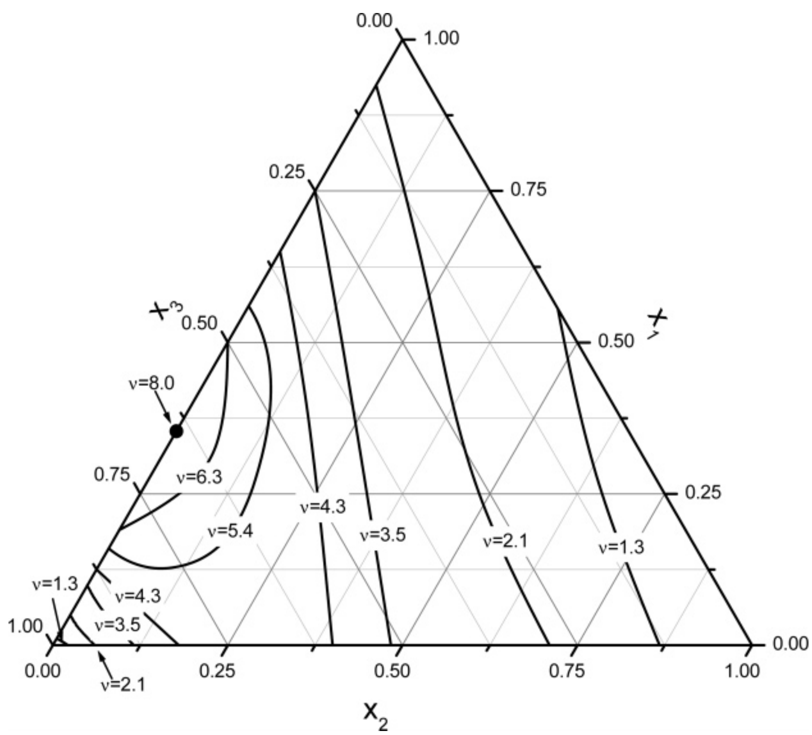

Figure 2. Influence of mixture composition on kinematic viscosity for pyrrolidine (1) + piperidine (2) + water (3) system.

an accuracy of ± 0.01 s was used for measuring efflux times. The capillary viscometer was immersed in a liquid bath, which can control the temperature within ± 0.1 °C. Each measurement was repeated at least five times. The absolute viscosity η was obtained from the product of kinematic viscosity ν and the corresponding density ρ of the mixture, in terms of eq 2 for each temperature and mixture composition.

$$\eta = \rho \cdot \nu \qquad (2)$$

The surface tension was measured by using a Krüss K-11 tensiometer and the Wilhelmy plate method. The plate employed was a commercial platinum plate supplied by Krüss. The platinum plate was cleaned and flame-dried before each measurement. The surface tension of pure water was determined to confirm the method. The uncertainty of the measurement was $\pm\ 3 \cdot 10^{-2}$ $mN \cdot m^{-1}$. In general, each surface tension value reported was an average of 10 measurements. The samples were thermostated in a closed vessel with stirring, before surface

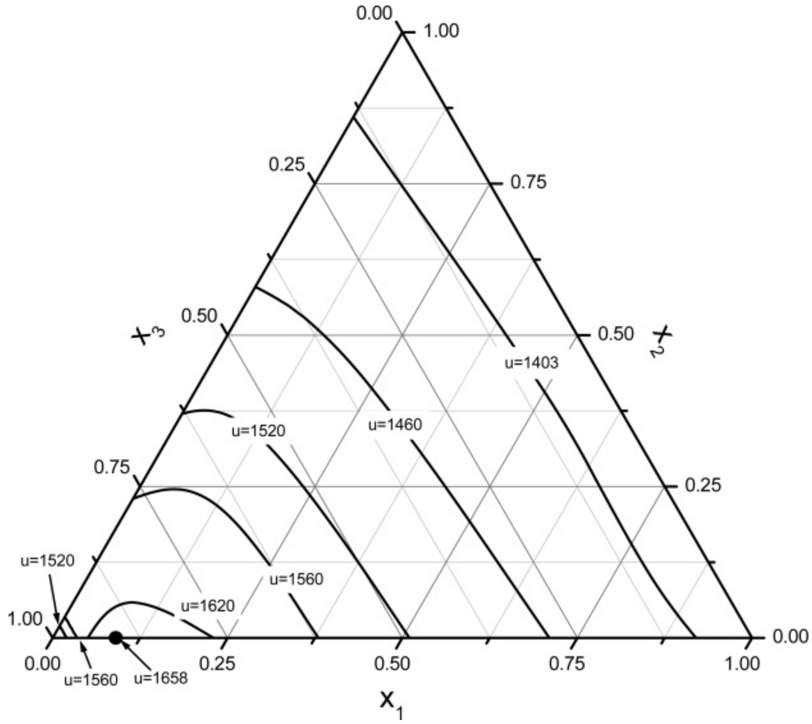

Figure 3. Influence of mixture composition on speed of sound for pyrrolidine (1) + piperidine (2) + water (3) system.

tension measurements. Surface tension measurements were carried out at 20 ± 0.1 °C.

Results and Discussion

Table 1 shows a comparison between experimental values of different physicochemical properties determined in the present work for pure amines and corresponding bibliographic ones and indicates the validity of experimental methods employed in the present study.

The values reported in the present paper for all physicochemical properties (density, viscosity, speed of sound, and surface tension) at different amine mole fractions are listed in Table 2 for the piperidine + pyrrolidine system. This binary system has not been studied previously, but the values of different physicochemical properties of aqueous solutions of both amines have been published previously. The experimental values of density, kinematic viscosity, speed of sound, and surface tension for the ternary system (piperidine + pyrrolidine + water) are given in Table 3.

Figure 1 shows the experimental results by growing values of density isolines obtained in the present work. The behavior observed for this physical property shows a continuous increase in the value of density when the water content in the ternary system increases. The same behavior was found when surface tension experimental data were analyzed. For surface tension a large decrease was observed at low amine concentration such as the behavior obtained for aqueous solutions of both amines.[13]

In relation with the other two physicochemical properties determined and analyzed in the present work (kinematic viscosity and speed of sound), the behaviors observed were quite different from the previous ones described for density and surface tension. For kinematic viscosity (Figure 2) and speed of sound (Figure 3) a maximum was obtained in a binary mixture and more specifically in the pyrrolidine + water mixture. The ternary graphs show this behavior by means of lines of constant values. These behaviors are in agreement with the aqueous binary systems previously studied in relation with the effect of composition upon kinematic viscosity and speed of sound.[8,14]

The values of excess molar volumes and changes in the physicochemical properties (ΔY) were calculated using the equations

$$V^{E} = \sum_{i=1}^{3} x_i \cdot M_i \cdot (\rho^{-1} - {\rho_i}^{-1}) \tag{3}$$

$$\Delta Y = Y - \sum_{i=1}^{3} x_i \cdot Y_i \tag{4}$$

where x_i, M_i, ρ_i, and Y_i are the molar fractions, molecular weights, densities, and physicochemical properties of pure components, respectively.

The deviation values were correlated as a function of composition using the Redlich−Kister equation for ternary systems (eq 5)

$$\Delta Y_{123} = \Delta Y_{12} + \Delta Y_{13} + \Delta Y_{23} + x_1 \cdot x_2 \cdot x_3 \cdot (A + B \cdot x_1 + C \cdot x_2) \tag{5}$$

where ΔY_{123} is the deviation considered, x_i is the mole fraction of component i, and ΔY_{ij} is the value of the Redlich−Kister polynomial for the same property fitted to the data for the corresponding binary system determined by equation (eq 6).[15]

$$\Delta Y = x_1 x_2 \sum_{j=1}^{4} q_j {x_2}^{(j-1)/2} \tag{6}$$

Table 3. Density, Viscosity, Speed of Sound, and Surface Tension of Ternary Mixtures of Piperidine (1) + Pyrrolidine (2) + Water (3)

x_1	x_2	ρ/g·cm^{-3}	η/mPa·s	u/m·s^{-1}	σ/mN·m^{-1}
0.9497	0.0302	0.86176	0.8513	1392.7	30.38
0.9004	0.0597	0.86301	0.8961	1395.0	30.28
0.8522	0.0886	0.86431	0.9346	1397.5	30.50
0.8129	0.0886	0.86726	1.0042	1403.9	30.81
0.7972	0.1448	0.86455	0.9533	1397.7	30.49
0.7587	0.1447	0.86796	1.0352	1404.9	30.77
0.6324	0.2757	0.86792	1.0876	1403.6	30.84
0.6627	0.1444	0.87574	1.3718	1422.1	31.36
0.5175	0.3947	0.86832	1.1543	1402.9	30.98
0.5411	0.2752	0.87658	1.4565	1422.3	31.37
0.5671	0.1442	0.88396	1.6649	1442.7	31.62
0.4125	0.5035	0.86727	1.3070	1400.3	30.23
0.4305	0.3941	0.87509	1.4964	1418.2	31.02
0.4502	0.2747	0.88427	1.8461	1441.0	31.58
0.4718	0.1440	0.89436	2.1855	1468.2	32.09
0.3163	0.6032	0.86769	1.4031	1399.6	30.50
0.3295	0.5027	0.87567	1.6248	1417.5	30.85
0.3439	0.3935	0.88443	2.2299	1438.7	31.17
0.3596	0.2743	0.89446	2.6888	1464.9	32.10
0.3768	0.1437	0.90621	2.8889	1497.0	32.75
0.2278	0.6949	0.86820	1.5400	1398.9	30.55
0.2369	0.6023	0.87612	1.8144	1416.2	30.89
0.2468	0.5020	0.88502	2.4935	1437.3	31.58
0.2575	0.3929	0.89501	2.7324	1462.6	32.06
0.2692	0.2738	0.90650	3.4339	1492.9	33.39
0.2821	0.1435	0.91944	3.8814	1527.9	34.29
0.1460	0.7797	0.86852	1.6330	1397.6	30.21
0.1516	0.6940	0.87645	1.9755	1414.5	30.74
0.1577	0.6015	0.88508	2.6439	1434.4	30.94
0.1643	0.5012	0.89511	3.1985	1459.1	31.86
0.1714	0.3923	0.90641	3.9671	1487.7	32.65
0.1792	0.2734	0.91905	4.5750	1520.4	33.74
0.1877	0.1432	0.93476	5.2004	1560.4	34.42
0.0703	0.8581	0.86923	1.9815	1396.9	30.27
0.0729	0.7786	0.87686	2.2197	1412.7	30.65
0.0757	0.6930	0.88601	2.8850	1433.1	30.84
0.0787	0.6006	0.89514	3.6350	1455.8	31.96
0.0820	0.5005	0.90682	4.9897	1483.2	32.57
0.0856	0.3917	0.91149	5.6461	1513.9	33.39
0.0895	0.2730	0.93470	6.1538	1549.6	34.07
0.0937	0.1430	0.94318	5.4118	1588.5	35.07
0.0428	0.9137	0.86637	1.8039	1390.4	30.27
0.0281	0.9433	0.86682	1.8103	1390.9	30.55
0.0757	0.1154	0.95813	5.2652	1599.7	35.77
0.0573	0.0874	0.96865	4.5682	1614.6	36.44
0.0385	0.0588	0.98195	3.4382	1623.9	37.60
0.0195	0.0297	0.99071	2.3183	1616.7	39.79

The calculated parameters corresponding to fit composition/properties values to the Redlich−Kister equation are listed in Table 4. Also, the root-mean-square deviations (δ) were calculated by means of eq 7.

$$\delta = \left(\frac{\sum_i (z_{\text{exptl}} - z_{\text{calcd}})^2}{n_{\text{data}}} \right)^{1/2} \quad (7)$$

Table 4. Coefficients of the Redlich−Kister Type Equation and Root-Mean-Square Deviations δ

	A	B	C	δ
V^E/cm^3·mol^{-1}	35.1	−54.5	−39.8	0.24
$\Delta\eta$/mPa·s	−8.1	17.9	−61.1	0.44
$\Delta\sigma$/mN·m^{-1}	−90.5	127.5	116.6	3.3
ΔK_s·10^{12}/Pa^{-1}	−1949	−229.8	3638	28.6

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