Densities and Viscosities of Aqueous Solutions of Pyrrolidine and Piperidine from (20 to 50) °C

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In the present paper, density and kinematic viscosity have been determined for aqueous solutions of two amines (pyrrolidine and piperidine) at (20, 30, 40, and 50) °C. The study of these mixtures has covered its complete composition range. Density shows the typical behavior of the composition and temperature's effect, but viscosity shows a maximum with an increased amine composition. A Redlich−Kister type equation was employed to fit the excess properties.

Introduction

In the past decades, amines and their mixtures 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 these gases and the amines.[1,2] Certain aqueous solutions of amines remove selectively acid gases present in the mixtures, for example, monoethalamine (MEA), *N*-methyldiethanolamine (MDEA), or triethanolamine (TEA).[3]

The use of these aqueous solutions as an absorbent involves the knowledge of physical properties of these systems (i.e., gas−liquid diffusivity)[4] since they are used to calculate essential parameters when analyzing absorption processes. For this reason, it is important to know their behavior in relation to the operational variables: mixture composition and temperature. Several studies[4] have been aimed at studying the effect of physical properties upon processes such as carbon dioxide absorption in amines aqueous solutions.

Other authors have analyzed in previous papers different amine + water systems in relation to important physical properties with influence in several industrial operations.[5,6] Densities, viscosities, and thermal conductivity have been measured for aqueous solutions of different amines and alkanolamines. The physical properties determined in the present paper have also been measured in the range of temperature from (20 to 50) °C to cover the temperature range found in industrial applications.

Nowadays, different types amines have been employed to remove acid gases;[7] piperazine, for example, is one of the amines with importance in these studies.[8] Aqueous solutions of pyrrolidine have also been employed as liquid absorbent to remove carbon dioxide.[9] Related to the amines used in the present paper, Minevich and Marcus[10] have developed studies related to the density behavior of pyrrolidine aqueous solutions at 25 and 50 °C. Teitel'baum et al.[11] have also developed experimental studies in the water + piperidine system, determining density, viscosity, surface tension, and refractive index of this binary mixture at 0, 25, 50, and 75 °C. In this work, the behavior for density and viscosity has been determined for aqueous solutions of pyrrolidine and piperidine over the entire concentration range at temperatures from 20 to 50 °C. In a previous paper, our research team had measured the surface tension of aqueous solutions of these amines aqueous solutions.[12]

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 %. Double-distilled 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 uncertainty of the samples preparation in mole fraction was ± 0.0004.

Methods. Density (ρ) of the pure liquids and its mixtures was measured with an Anton Paar DSA 5000 vibration tube densimeter with a precision of ± 10^{-6} g·cm^{-3}. The apparatus allows varying the temperature in the range used in the present study. The uncertainty in the density measurement was ± $5 \cdot 10^{-5}$ g·cm^{-3}.

The kinematic viscosity (ν) was determined from the transit time of the liquid meniscus through a capillary supplied by Schott (cap no. 0c, (0.46 ± 0.01) mm of internal diameter, K = 0.003201 mm^2·s^{-2}) measured with an uncertainty of ± 0.0005 mm^2·s^{-1} using

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

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 Ubbelohde viscometer. An electronic stopwatch with an accuracy of ± 0.01 s was used for measuring efflux times. The capillary viscometer was immersed in a bath controlled to ± 0.1 °C. Each measurement was repeated at least five times. The dynamic viscosity (η) was obtained from the product of kinematics' viscosity (ν) and the corresponding density (ρ) of the binary mixture, in terms of eq 2 for each temperature and mixture composition:

$$\eta = \rho \cdot \nu \tag{2}$$

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Table 1. Density (ρ) for Water (1) + Pyrrolidine (2) from t = 20 °C to 50 °C

	ρ/(g·cm^{-3}) at t/°C			
x_2	20	30	40	50
1.0000	0.85987	0.85011	0.84024	0.83388
0.8675	0.87239	0.86269	0.85281	0.84630
0.6858	0.89317	0.88353	0.87370	0.86368
0.5671	0.90610	0.89600	0.88620	0.87770
0.4834	0.91704	0.90758	0.89792	0.88805
0.3958	0.92864	0.91934	0.90983	0.90011
0.3039	0.94339	0.93433	0.92506	0.91560
0.2076	0.96231	0.95357	0.94465	0.93551
0.1158	0.98095	0.97319	0.96526	0.95715
0.0678	0.98946	0.98341	0.97691	0.97003
0.0221	0.99447	0.99112	0.98692	0.98200
0.0101	0.99633	0.99349	0.98978	0.98531
0.0057	0.99713	0.99441	0.99083	0.98646
0.0000	0.99821	0.99565	0.99221	0.98802

Table 2. Density (ρ) for Water (1) + Piperidine (2) from t = 20 °C to 50 °C

	ρ/(g·cm^{-3}) at t/°C			
x_2	20	30	40	50
1.0000	0.86381	0.85450	0.84508	0.83556
0.8454	0.87508	0.86574	0.85627	0.84667
0.6458	0.89299	0.88365	0.87416	0.86451
0.5225	0.90651	0.89728	0.88784	0.87822
0.4387	0.91750	0.90800	0.89900	0.88900
0.3536	0.92785	0.91889	0.90973	0.90037
0.2672	0.94018	0.93155	0.92271	0.91366
0.1795	0.95567	0.94760	0.93932	0.93084
0.0986	0.97458	0.96757	0.96035	0.95286
0.0573	0.98556	0.97956	0.97325	0.96660
0.0280	0.99243	0.98787	0.98266	0.97692
0.0110	0.99589	0.99289	0.98903	0.98442
0.0055	0.99707	0.99434	0.99068	0.98617
0.0000	0.99821	0.99565	0.99221	0.98802

Table 3. Kinematic Viscosity (ν) for Water (1) + Pyrrolidine (2) from t = 20 °C to 50 °C

	ν/(mm^2·s^{-1}) at t/°C			
x_2	20	30	40	50
1.0000	0.9545	0.8268	0.7432	0.6412
0.8675	1.312	1.067	0.9134	0.7842
0.6858	2.133	1.706	1.368	1.119
0.5671	2.994	2.236	1.764	1.393
0.4834	3.639	2.733	2.085	1.605
0.3958	4.356	3.131	2.307	1.790
0.3039	4.776	3.343	2.457	1.866
0.2076	4.528	3.154	2.272	1.728
0.1158	3.518	2.419	1.770	1.364
0.0678	2.471	1.763	1.342	1.063
0.0221	1.438	1.121	0.8805	0.7629
0.0000	0.9899	0.8101	0.6655	0.5610

Results and Discussion

The values determined in the present paper for all physical studies at different amine concentrations and temperatures in the range between 20 and 50°C are listed in Tables 1 and 3 for the water + pyrrolidine system and in Tables 2 and 4 for the water + piperidine system. 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. As regards the effect caused by mixture composition, the presence of amines in the aqueous solutions produces an increase when the pyrrolidine and piperidine composition increases in the mixture (see Figure 1). The behavior observed in the present paper is very common and similar to the results obtained by other authors for water/amine systems.[13]

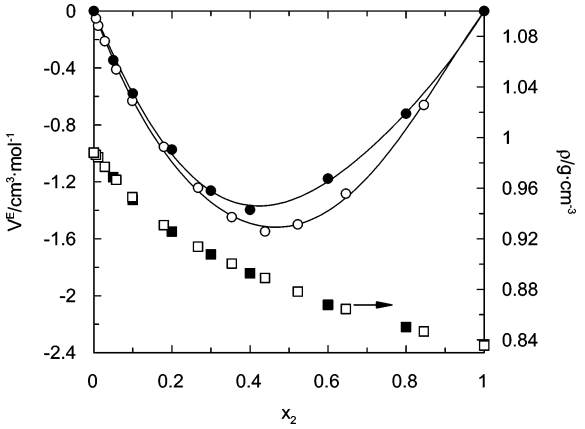

Figure 1. Density and excess volume for water (1) + piperidine (2) system: ○ and □, present paper; ● and ■, Teitel'baum et al.[11]

Table 4. Kinematic Viscosity ν, for Water (1) + Piperidine (2) from t = 20 °C to 50 °C

	ν/(mm^2·s^{-1}) at t/°C			
x_2	20	30	40	50
1.0000	1.795	1.488	1.253	1.064
0.8455	2.598	1.997	1.621	1.315
0.6458	4.490	3.220	2.333	1.832
0.5225	6.088	4.371	3.104	2.311
0.4387	7.036	4.968	3.488	2.526
0.3536	8.023	5.417	3.705	2.680
0.2672	7.621	5.058	3.480	2.616
0.1795	5.936	4.007	2.813	2.139
0.0986	3.550	2.553	1.881	1.470
0.0573	2.200	1.741	1.325	1.066
0.0280	1.502	1.205	0.9421	0.8125
0.0110	1.210	0.9527	0.7723	0.6363
0.0055	1.106	0.8817	0.7181	0.5981
0.0000	0.9899	0.8101	0.6655	0.5610

Table 5. Density (ρ) and Viscosity (η) of Pure Piperidine and Pyrrolidine

piperidine			pyrrolidine		
t/(°C)	ρ/(g·cm^{-3})	η/(mPa·s)	t/(°C)	ρ/(g·cm^{-3})	η/(mPa·s)
20	0.8638[a]	1.5506[a]	20	0.8599[a]	0.8207[a]
	0.8606[b]	1.559[c]		0.8586[b]	0.799[c]
	0.862[c]			0.864[c]	
50	0.8356[a]	0.8887[a]		0.856[d]	
	0.8336[c]	0.958[b]	50	0.8339[a]	0.5347[a]
	0.8366[e]	0.910[c]		0.836 [c]	0.512[b]
		0.757[e]		0.8346[f]	0.521[c]

[a] Present paper. [b] Ref 14. [c] Ref 15. [d] Ref 16. [e] Ref 11. [f] Ref 10.

Table 5 shows a comparison between the experimental results obtained by our research group and the bibliographical results obtained by other researchers and included in some handbooks. Low deviations can be observed in the aforementioned table as regards most of the bibliographical results.

The presence of pyrrolidine and piperidine makes the viscosity to reach a maximum value of about an amine mole fraction of 0.3. A high value in the kinematic and absolute viscosity is observed in the maximum previously commented, as regards the value of this physical property (viscosity) for the pure components that have similar values (ν_{water} = 0.9899 mm^2·s^{-1}; $\nu_{pyrrolidine}$ = 0.9545 mm^2·s^{-1}; $\nu_{piperidine}$ = 1.7950 mm^2·s^{-1} at 20 °C). Other authors have found a similar behavior for aqueous solutions of ethanolamine.[17] Regarding the effect of temperature, this variable causes a clear decrease in the viscosity values for all the water + amine systems analyzed.

Table 6. Fit Parameters Corresponding to the Redlich−Kister Equation for Aqueous Solutions of Piperidine at Several Temperatures (20 to 50 °C)

	t/°C			
	20	30	40	50
	V^E/(cm^3·mol^{-1})			
q_1	−6.302	−6.199	−6.147	−6.045
q_2	1.018	0.9358	0.9275	0.8711
q_3	0.0549	0.1848	0.3784	0.3896
q_4	1.156	1.271	1.023	0.9353
	$\Delta\eta$/(mPa·s)			
q_1	9.479	6.605	4.692	3.411
q_2	−16.83	−10.68	−6.954	−4.777
q_3	6.522	3.277	1.860	1.449
q_4	6.042	3.841	2.118	1.220

Table 7. Fit Parameters Corresponding to the Redlich−Kister Equation for Aqueous Solutions of Pyrrolidine at Several Temperatures (20 to 50 °C)

	t/°C			
	20	30	40	50
	V^E/(cm^3·mol^{-1})			
q_1	−6.639	−6.554	−6.515	−5.752
q_2	0.2554	0.1851	0.0541	0.6144
q_3	−1.230	−1.122	−0.9502	−1.432
q_4	2.614	2.232	2.121	0.627
	$\Delta\eta$/(mPa·s)			
q_1	18.74	12.41	8.052	5.519
q_2	−30.95	−18.54	−11.71	−7.449
q_3	−0.6133	−1.250	−0.2604	0.5126
q_4	30.23	15.98	9.714	5.490

The excess molar volumes (V^E) and viscosity deviations ($\Delta\eta$) were calculated using

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

where Y_m is the value of the physical property considered for the mixture, and Y_1, Y_2, x_1, and x_2 are the values of the physical properties and mole fraction for pure components, respectively.

The values calculated for viscosity deviations and excess molar volumes were fitted using a Redlich−Kister type equation (eq 4):

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

The results obtained for fitting parameters are shown in Tables 6 and 7.

The Redlich−Kister equation fits satisfactorily (Figures 1 and 2) the deviation values calculated from experimental data of density and viscosity. When we analyzed the results obtained concerning the influence of mixture composition upon the excess volumes (Figure 1), we can observe that these deviations are negative in all cases. As regards the excess volume value, certain deviation can be observed when comparing it to the values that had been calculated by means of the experimental data obtained by Teitel'baum et al. [11]

These negative deviations indicate that there are interactions among unlike molecules. On the basis of deviations' sign and magnitude (large deviations), we consider that there are strong hydrogen bonding interactions in the mixtures studied in the present paper. According to previous studies developed by Kapadi et al.,[17] negative values for excess volume could be due to (i) the reaction between water and amine compound where the amine is protoned and (ii) the reaction between two molecules of amine forming a species-charged positive and negatively. In relation to the effect of temperature upon the excess volume, experimental data indicate that when the temperature value increases, the excess volume increases too.

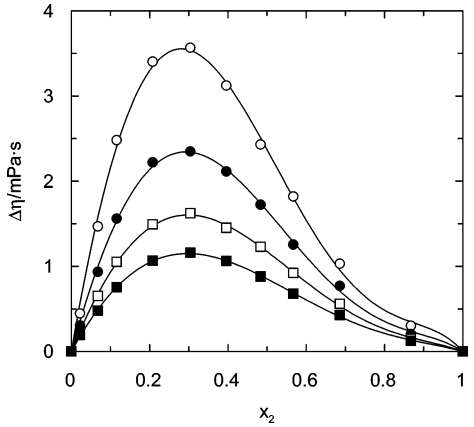

Figure 2. Absolute viscosity deviations for water (1) + pyrrolidine (2) system: ○, t = 20 °C; ●, t = 30 °C; □, t = 40 °C; ■, t = 50 °C.

The influence of mixture composition upon the value of absolute viscosity deviations, shown in Figure 2, indicates that all the mixtures formed by water and pyrrolidine have positive deviations. A similar behavior was observed for the other mixture studied in the present work. Great differences have been found when experimental data were compared with that previously obtained by Teitel'baum et al.[11] We consider that perhaps these differences are due to viscosity determination procedure because of the great differences observed in Table 5 for pure component (piperidine). The same conclusion has been obtained for viscosity deviations (hydrogen-bonding interactions between water and amine molecules) when excess volume was analyzed. The temperature causes a decrease in the value of the viscosity deviations.

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Literature Cited

(1) Fathi, J.; Baheri, H. R. Amine plant simulation by mass transfer and kinetic approach. *Chem. Eng. Technol*. **1995**, *18*, 397−402.
(2) Xu, S.; Wang, Y.-W.; Otto, F. D.; Mather, A. E. Kinetics of the reaction of carbon dioxide with 2-amino-2-methyl-1-propanol solutions. *Chem. Eng. Sci*. **1996**, *51*, 841−850.
(3) Rangwala, H. A.; Morrell, B. R.; Mather, A. E.; Otto, F. D. Absorption of carbon dioxide into aqueous tertiary amine/MEA solutions. *Can. J. Chem. Eng*. **1992**, *70*, 482−490.
(4) Camacho, F.; Sánchez, S.; Pacheco, R. Absorption of carbon dioxide at high partial pressures in 1-amino-2-propanol aqueous solution. Considerations of thermal Effects. *Ind. Eng. Chem. Res.* **1997**, *36*, 4358−4364.
(5) 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.
(6) Hsu, C.-H.; Li, M.-H. Viscosities of aqueous blended amines. *J. Chem. Eng. Data* **1997**, *42*, 714−720.
(7) Cullinane, J. T.; Rochelle, G. T. Carbon dioxide absorption with aqueous potassium carbonate promoted by piperazine. *Chem. Eng. Sci*. **2004**, *59*, 3619−3630.
(8) Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A.; Smith, N. K. Thermodynamic properties and ideal-gas enthalpies of formation for dicyclohexyl sulfide, diethylenetriamine, di-*n*-octyl sulfide, dimethyl carbonate, piperazine, hexachloroprop-1-ene, tetrakis(dimethylamino)ethylene, *N*,*N*′-bis-(2-hydroxyethyl)ethylenediamine, and 1,2,4-triazolo[1,5-a]pyrimidine. *J. Chem. Eng. Data* **1997**, *42*, 1037−1052.
(9) 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.
(10) 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.
(11) Teitel'baum, B. Ya.; Trifonov, N. A.; Khachatur'yan, V. R. Physicochemical analysis of the system water-piperidine. *Zh. Fiz. Khim.* **1947**, *21*, 503−508.
(12) Gómez-Díaz, D.; Navaza, J. M. Surface behavior of aqueous solutions of pyrrolidine and piperidine. *J. Chem. Eng. Data* **2004**, *49*, 1406−1409.
(13) Chan, C.; Maham, Y.; Mather, A. E.; Mathonat, C. Densities and volumetric properties of the aqueous solutions of 2-amino-2-methyl-1-propanol, *n*-butyldiethanolamine and *n*-propylethanolamine at temperatures from 298.15 to 353.15 K. *Fluid Phase Equilib*. **2002**, *198*, 239−250.
(14) Lide, D. R. *CRC Handbook of Chemistry and Physics: A Ready-Reference Book of Chemical and Physical Data*; CRC Press: Boca Raton, FL, 2002.
(15) Yaws, C. L. *Chemical Properties Handbook Physical, Thermodynamic*, *Environmental, Transport, Safety and Health Related Properties for Organic and Inorganic Chemicals*; McGraw-Hill: London, 1999.
(16) Rappoport, Z. *Handbook of Tables for Organic Compounds Identification*. The Chemical Rubber: Boca Raton, FL, 1967.
(17) Kapadi, U. R.; Hundiwale, D. G.; Patil, N. B.; Lande, M. K. Viscosities, excess molar volume of binary mixtures of ethanolamine with water at 303.15, 308.15, 313.15 and 318.15 K. *Fluid Phase Equilib*. **2002**, *201*, 335−341.

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