Density and Viscosity of Aqueous Solutions of Piperazine and (2-Amino-2-methyl-1-propanol + Piperazine) from 298 to 333 K

Arunkumar Samanta and Syamalendu S. Bandyopadhyay*

Separation Science Laboratory, Cryogenic Engineering Centre, Indian Institute of Technology, Kharagpur 721 302, India

The densities and viscosities of aqueous solutions of piperazine (PZ) and aqueous blends of 2-amino-2-methyl-1-propanol (AMP) and piperazine have been measured at (298, 303, 308, 313, 318, 323, 328, and 333) K. The experiments covered the concentration range of (0.2 to 0.8) mol·L^{-1} piperazine (mass fraction piperazine (1.74 to 6.88) %) for the (PZ + water) system and mass fraction of (2 to 8) % for piperazine-activated blended AMP solutions. The results are compared with the available data in the literature. The experimental density and viscosity data were correlated as a function of temperature and concentration of amine.

Introduction

The removal of acid gas impurities, such as CO_2 and H_2S from industrial gases is an essential step in processing sour natural gas streams, refinery off-gases, and synthesis gas for ammonia production. A widely practiced process for the removal of CO_2 and H_2S from sour gas streams is the regenerative absorption of the acid gases into aqueous alkanolamine solvents. Traditionally, monoethanolamine (MEA), diethanolamine (DEA), and *N*-methyldiethanolamine (MDEA) have been used industrially for the removal of CO_2 from natural gas and industrial gas streams.[1] Recently, a new class of amine, the sterically hindered amines (e.g., 2-amino-2-methyl-1-propanol; AMP), has been suggested as attractive solvents for removal of acid gases from industrial gas streams due to their higher CO_2 absorption capacity than the conventional primary and secondary amines, such as MEA and DEA.[2] The reaction of CO_2 with aquesous solutions of AMP has been studied extensively by several researchers.[3−6] A recent advancement in gas-treating technology is the application of blended amines, which offer enhanced absorption capacity and absorption rate and reduced solvent regeneration energy.[7] Blends of primary and tertiary amines or secondary and tertiary amines have been already suggested for the industrial gas-treating processes.[1,7] While aqueous piperazine (PZ) and blended solvent piperazine-activated aqueous AMP solutions can be potentially high efficiency solvents for CO_2 removal, these solvent systems have not been investigated so far. Piperazine is used as an activator in BASF-activated MDEA technology,[8] and it is reported that piperazine is more effective than the conventional accelerators. Being a cyclic symmetric diamine in a six-membered saturated ring, piperazine can theoretically absorb 2 mol of CO_2 for every mol of amine, and it may favor rapid formation of the carbamates. The rate constant of PZ has been found to be 1 order higher than that of conventional alkanolamines such as MEA.[9]

Knowledge of the physical properties, for example, density and viscosity, of aqueous piperazine as well as piperazine-activated solvents is essential for the process design of gas treating units and the design of gas treatment equipment for processes using these solvents. This is also essential for the measurement of other physicochemical properties such as diffusivities, free-gas solubilities, and reaction rate constants. Solution density and viscosity are also important for the mass transfer rate modeling of absorption and regeneration because these properties influence the values of the liquid side mass transfer coefficient, k_L. However, despite the immense importance of these data, few results are available in the open literature.

In this study, the density and viscosity of aqueous solutions of piperazine and aqueous blends of piperazine and AMP have been determined in the industrially important temperature range of (298 to 333) K. The experiments covered the commercially significant concentration range of (0.2 to 0.8) mol·L^{-1} piperazine (mass fraction piperazine (1.74 to 6.88) %). The density and viscosity data were correlated as function of temperature and concentration of amine.

Experimental Section

Piperazine (> 99 % pure) and AMP (> 97 % pure) were obtained from E. Merck, FRG, and were used without further purification. Distilled water degassed by boiling was used for preparing the amine solutions. The amine concentration was determined by titration against 0.5 mol·L^{-1} HCl using methyl orange indicator.

Density. The densities of aqueous amine solutions were measured by using a 25.78 mL (at 298 K) Gay-Lussac pycnometer. For each run the pycnometer containing the amine solution was put in a constant-temperature bath. The bath temperature was controlled within ± 0.1 K of the desired temperature using a circulator temperature controller (JULABO F 32, FRG). Once the solution reached the desired temperature, it was weighed to within ± 0.0001 g with an analytical balance (ACCULAB-ALC 210.4, FRG). Each reported density data is the average of at least five measurements. The density of water is adopted directly from Perry's Handbook.[10] The probable uncertainty in the measured density is about ± 4.5 × 10^{-5} g·cm^{-3}.

Viscosity. The viscosities of aqueous amine solution were measured using an Ostwald viscometer. For each viscosity measurement, the temperature was controlled within ± 0.1 K of the desired level with a circulator temperature controller. Each viscosity data is the average of at least five measurements.

* Corresponding author. Telephone: +91-3222-83580. Fax: +91-3222-282258. E-mail: ssbandyo@hijli.iitkgp.ernet.in.

10.1021/je050378i CCC: $33.50
Published on Web 02/04/2006

Table 1. Densities ρ for Piperazine (1) + Water (3) from 298 K to 333 K

	ρ/g·cm^{-3}							
$100w_1$	$T = 298.0$ K	$T = 303.0$ K	$T = 308.0$ K	$T = 313.0$ K	$T = 318.0$ K	$T = 323.0$ K	$T = 328.0$ K	$T = 333.0$ K
1.74	0.9978	0.9965	0.9951	0.9932	0.9914	0.9893	0.9867	0.9842
3.45	0.9985	0.9972	0.9957	0.9941	0.9922	0.9902	0.9874	0.9845
5.16	0.9994	0.9981	0.9965	0.9947	0.9925	0.9904	0.9880	0.9857
6.88	1.0006	0.9990	0.9976	0.9956	0.9938	0.9914	0.9891	0.9874

Table 2. Densities ρ for Piperazine (1) + 2-Amino-2-methyl-1-propanol (2) + Water (3) from 298 K to 333 K

	ρ/g·cm^{-3}							
w_2/w_1	$T = 298.0$ K	$T = 303.0$ K	$T = 308.0$ K	$T = 313.0$ K	$T = 318.0$ K	$T = 323.0$ K	$T = 328.0$ K	$T = 333.0$ K
30/0	0.9970	0.9942	0.9914	0.9884	0.9854	0.9821	0.9788	0.9755
28/2	0.9987	0.9959	0.9931	0.9903	0.9871	0.9838	0.9807	0.9770
25/5	1.0010	0.9984	0.9956	0.9926	0.9895	0.9865	0.9831	0.9799
22/8	1.0037	1.0010	0.9982	0.9950	0.9922	0.9889	0.9858	0.9824

Table 3. Parameters and AADs for Density Correlations for Piperazine (1) + Water (3) and Piperazine (1) + 2-Amino-2-methyl-1-propanol (2) + Water (3)

	A_i	B_i	C_i
		PZ + H_2O	
$i = 0$	0.7550	1.8866×10^{-3}	-3.6056×10^{-6}
$i = 1$	3.1716×10^{-4}	7.0006×10^{-7}	-6.1337×10^{-10}
$i = 2$	3.5437×10^{-5}	-1.7548×10^{-7}	2.2115×10^{-10}
S_1		0.0	
S_2		1.0	
AAD		0.0001665	
		AMP + PZ + H_2O	
$i = 0$	0.7550	1.8866×10^{-3}	-3.6056×10^{-6}
$i = 1$	1.0652×10^{-3}	1.4484×10^{-5}	-4.8522×10^{-6}
$i = 2$	2.2700×10^{-4}	-1.9284×10^{-6}	3.5101×10^{-9}
S_1		1.0	
S_2		−0.00315	
AAD[a]		0.0002203	

[a] $$\text{AAD} = \frac{1}{N}\sum_{i=1}^{N}\frac{|\rho_{\text{calcd},i} - \rho_{\text{exptl},i}|}{\rho_{\text{exptl},i}}$$

Values of the viscosity of water were taken from Geankoplis.[11] The estimated uncertainty in viscosity measurement 1.0 %.

Results and Discussion

Density. The measured densities of the solutions of (PZ + H_2O) and (AMP + PZ + H_2O) are presented in Tables 1 and 2, respectively. For aqueous solutions of mass fraction of 30 % AMP, the deviation is 0.04 % when compared with the experimental data of Li and Lie.[12] The experimental density data of the binary and ternary mixtures were correlated as function of temperature and concentration of amine according to

$$\rho = \sum_{i=0}^{2}[A_i W^i + B_i W^i (T/\text{K}) + C_i W^i (T/\text{K})^2] \qquad (1)$$

where ρ is the density of the mixture; T is the temperature of mixture; A, B, and C are the correlation parameters; and W is the (total mass fraction of amine) × 100 in the solution. W is expressed as

$$W = \sum_{i=1}^{n}[S_i w_i] \qquad (2)$$

where w_i is the mass fraction of individual amine and S_i is the weighting factor for each amine. The calculated parameters and average absolute deviations (AADs) are listed in Table 3. The calculated densities from the correlation (eq 1) are in excellent agreement with the experimental data of this study; the average absolute deviations (AADs) between the correlated and experimental data for (PZ + H_2O) and (AMP + PZ + H_2O) systems are about 0.00016 and 0.00022, respectively. The comparisons between the measured and correlated densities are also shown in Figures 1 and 2 for (PZ + H_2O) and (AMP + PZ + H_2O) systems, respectively. As shown in these figures, the densities of the binary and ternary mixtures decrease with increasing temperature and decreasing mass fraction of PZ in the mixture.

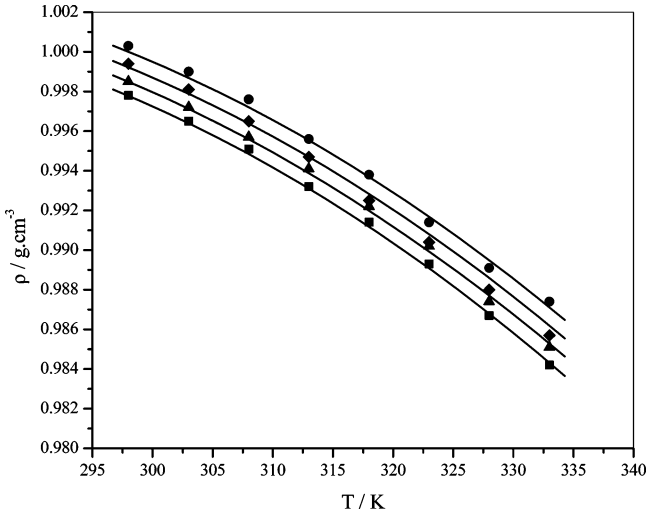

Figure 1. Density of PZ (1) + water (3) system at various temperatures: ●, $w_1 = 0.0688$; ◆, $w_1 = 0.0516$; ▲, $w_1 = 0.0344$; ■, $w_1 = 0.0174$. Lines are calculated by eq 1.

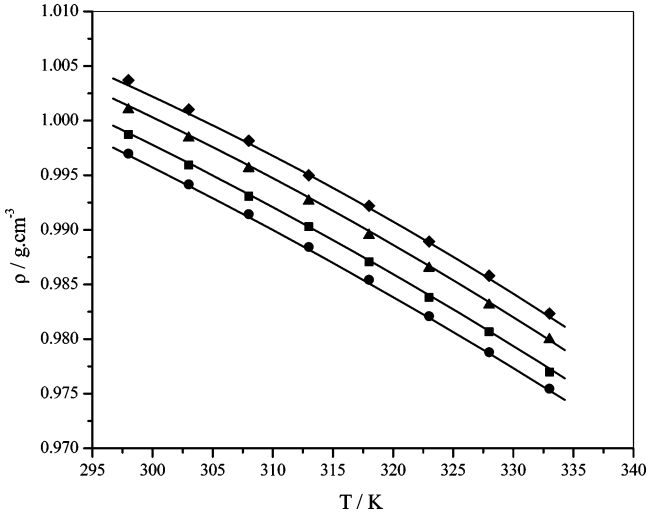

Figure 2. Density of PZ (1) + AMP (2) + water (3) system at various temperatures: ◆, $w_2/w_1 = 22/8$; ▲, $w_2/w_1 = 25/5$; ■, $w_2/w_1 = 28/2$; ●, $w_2/w_1 = 30/0$. Lines are calculated by eq 1.

Table 4. Viscosities η for Piperazine (1) + Water (3) from 298 K to 333 K

	η/mPa·s							
$100w_1$	$T = 298.0$ K	$T = 303.0$ K	$T = 308.0$ K	$T = 313.0$ K	$T = 318.0$ K	$T = 323.0$ K	$T = 328.0$ K	$T = 333.0$ K
1.74	0.957	0.861	0.776	0.681	0.623	0.573	0.543	0.488
3.44	1.021	0.915	0.805	0.718	0.652	0.592	0.543	0.505
5.16	1.090	0.965	0.865	0.763	0.703	0.624	0.569	0.523
6.88	1.169	1.035	0.910	0.821	0.731	0.663	0.604	0.546

Table 5. Viscosities η for Piperazine (1) + 2-Amino-2-methyl-1-propanol (2) + Water (3) from 298 K to 333 K

	η/mPa·s							
w_2/w_1	$T = 298.0$ K	$T = 303.0$ K	$T = 308.0$ K	$T = 313.0$ K	$T = 318.0$ K	$T = 323.0$ K	$T = 328.0$ K	$T = 333.0$ K
30/0	3.637	2.964	2.446	2.043	1.696	1.425	1.237	1.081
28/2	3.737	3.005	2.524	2.060	1.752	1.475	1.276	1.099
25/5	3.879	3.123	2.591	2.119	1.795	1.501	1.309	1.126
22/8	4.063	3.312	2.708	2.235	1.838	1.556	1.363	1.175

Table 6. Parameters and AADs for Viscosity Correlations for Piperazine (1) + Water (2) and Piperazine (1) + 2-Amino-2-methyl-1-propanol (2) + Water (3)

	A_i	B_i	C_i	D_i
		PZ + H_2O		
$i = 0$	−16.1096	0.1599	-2.1129×10^{-3}	2.4405×10^{-4}
$i = 1$	3405.7166	1.9515×10^{-3}	1.3307×10^{-3}	-3.1447×10^{-3}
$i = 2$	0.01538	-4.2813×10^{-4}	8.6945×10^{-6}	-6.6882×10^{-7}
S_1		0.0		
S_2		1.0		
AAD		0.0059		
		AMP + PZ + H_2O		
$i = 0$	−16.1096	0.0617	−0.4212	0.0133
$i = 1$	3405.7166	−0.2204	0.0234	0.1371
$i = 2$	0.01538	0.0469	-2.1581×10^{-3}	2.0604×10^{-5}
S_1		1.0		
S_2		1.0034		
AAD		0.006646		

Viscosity. Experimentally measured viscosities of the binary solutions of aqueous PZ and of the blended aqueous solutions of AMP and PZ for the temperature range (298 to 333) K are listed in Tables 4 and 5. On the basis of the experimental data, the following correlation has been developed:

$$\ln \eta = \Phi_1 + \frac{\Phi_2}{T} + \Phi_3 T \tag{3}$$

where η is the viscosity of the mixture, T is the temperature of mixture, and Φ_i values are the parameters and are expressed as

$$\Phi_i = a_i + b_i W + c_i W^2 + d_i W^3 \tag{4}$$

where W is the (total mass fraction of amine) × 100 in the solution and given in eq 2. Table 6 includes the determined parameters and AADs between the measured and calculated values for both (PZ + H_2O) and (AMP + PZ + H_2O) solvent systems. The average absolute deviations (AADs) between the correlated and experimental data for (PZ + H_2O) and (AMP + PZ + H_2O) systems are about 0.0059 and 0.0066, respectively. The small AAD values indicate that the calculated viscosities from eq 3 are in good agreement with the experimental results of this study. The measured and calculated viscosities from the correlation are also compared in Figures 3 and 4 for (PZ + H_2O) and (AMP + PZ + H_2O) systems, respectively. As shown in these figures, the viscosities of the binary and ternary mixtures decrease with increasing temperature and decreasing mass fraction of PZ in the mixture.

Conclusion

Densities and viscosities of (PZ + H_2O) and (AMP + PZ + H_2O) systems were measured and correlated over the temperature range (298 to 333) K. The mass fractions of piperazine for (PZ + H_2O) system were in the range (1.74 to 6.88) %. For blended amine system (i.e., for the (AMP + PZ + H_2O) system), the total amine mass fraction in the solution was kept at 30 %.The correlated densities and viscosities of the binary and

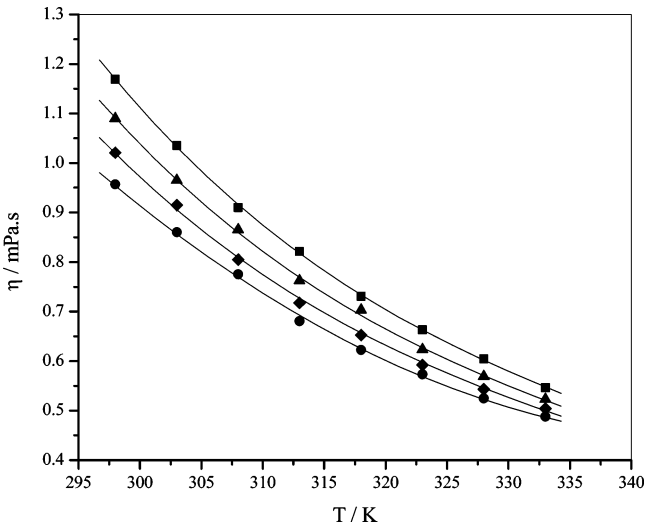

Figure 3. Viscosity of PZ (1) + water (3) system at various temperatures: ■, $w_1 = 0.0688$; ▲, $w_1 = 0.0516$; ◆, $w_1 = 0.0344$; ●, $w_1 = 0.0174$. Lines are calculated by eq 3.

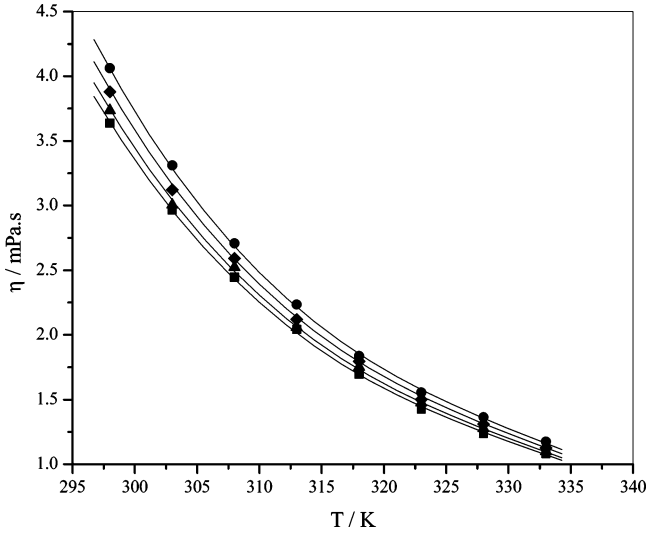

Figure 4. Viscosity of PZ (1) + AMP (2) + water (3) system at various temperatures: ■, $w_2/w_1 = 30/0$; ▲, $w_2/w_1 = 28/2$; ◆, $w_2/w_1 = 25/5$; ●, $w_2/w_1 = 22/8$. Lines are calculated by eq 3.

ternary mixtures are in excellent agreement with the experimental data over the temperature and amine concentration ranges studied.

Literature Cited

(1) Kohl, A. L.; Nielsen, R. B. *Gas Purification*, 5th ed.; Gulf Publishing Company: Houston, TX, 1997.

(2) Sartori, G.; Savage, D. W. Sterically hindered amines for CO_2 removal from gases. *Ind. Eng. Chem. Fundam.* **1983**, *22*, 239−249.

(3) Yih, S.-M.; Shen, K.-P. Kinetics of carbon dioxide reaction with sterically hindered 2-amino-2-methyl-1-propanol aqueous solutions. *Ind. Eng. Chem. Res.* **1988**, *27*, 2237−2241.

(4) Alper, E. Reaction mechanism and kinetics of aqueous solutions of 2-amino-2-methyl-1-propanol and carbon dioxide. *Ind. Eng. Chem. Res.* **1990**, *29*, 1725−1728.

(5) Saha, A. K.; Bandyopadhyay, S. S.; Biswas, A. K. Kinetics of absorption of CO_2 into aqueous solutions of 2-amino-2-methyl-1-propanol. *Chem. Eng. Sci.* **1995**, *50*, 3587−3598.

(6) 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.

(7) Chakravarty, T.; Phukan, U. K.; Weiland, R. H. Reaction of acid gases with mixtures of amines. *Chem. Eng. Prog.* **1985**, *81*, 32−36.

(8) Appl, M.; Wagner, U.; Henrici, H. J.; Kuessner, K.; Voldamer, K.; Fuerst, E. Removal of CO_2 and/or H_2S and/or COS from gases containing these constituents. U.S. Patent 4,336,233, 1982.

(9) Bishnoi, S.; Rochelle, G. T. Absorption of carbon dioxide into aqueous piperazine: reaction kinetics, mass transfer and solubility. *Chem. Eng. Sci.* **2000**, *55*, 5531−5543.

(10) Perry, R. H.; Chilton, C. H. *Chemical Engineer's Handbook*, 6th ed.; McGraw-Hill: New York, 1984.

(11) Geankoplis, C. J. *Transport Processes and Separation Process Principles*, 4th ed.; Prertice-Hall, Inc.: Englewood Cliffs, NJ, 2003.

(12) Li, M.-H.; Lie, Y.-C. Densities and viscosities of solutions of monoethanolamine + *N*-methyldiethanolamine + water and monoethanolamine + 2-amino-2-methyl-1-propanol + water. *J. Chem. Eng. Data* **1994**, *39*, 444−447.

Received for review September 16, 2005. Accepted December 27, 2005.

JE050378I