Density and Viscosity of Aqueous Solutions of (*N*-Methyldiethanolamine + Piperazine) and (2-Amino-2-methyl-1-propanol + Piperazine) from (288 to 333) K

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The densities and viscosities of aqueous blends of piperazine (PZ) with *N*-methyldiethanolamine (MDEA) and 2-amino-2-methyl-1-propanol (AMP) have been measured at (288, 293, 298, 303, 308, 313, 318, 323, 328, and 333) K. The total amine mass fraction in all solutions was kept at 30 % in view of recent interest in using concentrated amine solutions in gas treating. Correlations for the density and viscosity of the ternary mixtures are presented as a function of temperature and amine concentration.

Introduction

The removal of CO_2 from gaseous stream by absorption with chemical reaction in the liquid phase is usually employed in industry as a method to retain atmospheric CO_2 to combat the greenhouse effect. Industrially important alkanolamines are monoethanolamine (MEA), diethanolamine (DEA), di-2-propanolamine (DIPA), *N*-methyldiethanolamine (MDEA), and 2-amino-2-methyl-1-propanol (AMP).[1] The advantages of MDEA, a tertiary amine, include its high equilibrium loading capacity and its low heat of reaction with CO_2, which leads to lower energy requirement for regeneration. The CO_2 loading in AMP approaches a value equal to that in MDEA, while the reaction rate constant for CO_2−AMP is much higher than that for CO_2−MDEA.[2] Since AMP does not form stable carbamate, the regeneration energy costs may be lower as in the case of using aqueous MDEA solutions. Recently, piperazine (PZ) has been shown to be an effective promoter in MEA, MDEA, and potassium carbonate due to its rapid formation of carbamates with CO_2.[3−5] Under this situation, PZ would become a major component in the commercial absorption mixtures to capture CO_2 from flue gases of power generation plants.[6] The rate constant of PZ has been found to be one order higher than that of conventional alkanolamines such as MEA.[7] PZ-activated aqueous MDEA and AMP solutions combine the relatively high rate of reaction of the former with CO_2 with the lower heat of reaction of the later with CO_2. From these considerations, (MDEA + PZ + H_2O) and (AMP + PZ + H_2O) appear to be attractive new blended solvents for acid gas removal. While absorption of CO_2 into MDEA and AMP has been studied extensively in the past, only few publications have dealt with absorption of CO_2 into the blends of PZ with MDEA or AMP.[5,7−13] The density and viscosity data of aqueous blend of (AMP + PZ) are available in very few literatures.[9,14] However, the density and viscosity of aqueous blend of (MDEA + PZ) has not yet been published in the open literature so far.

In this work the density and viscosity of aqueous solutions of (MDEA + PZ) and (AMP + PZ) were measured over the temperature range (288 to 333) K. The total amine mass fraction in the solution was kept at 30 %. The density and viscosity of the ternary mixtures are correlated as a function of temperature and amine concentration.

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Experimental Section

Materials. Reagent grade piperazine (≥ 99 % pure), MDEA (> 98 % pure), and AMP (> 97 % pure) were obtained from E. Merck. Distilled water degassed by boiling was used for making the amine solutions. The total amine contents of the solutions were determined by titration with standard HCl using methyl orange indicator. The uncertainty in the composition of the amine solutions was estimated as ± 0.0002 g.

Density. The densities of the amine solutions were measured using a 26.76 mL Gay-Lussac pycnometer. The pycnometer containing the amine solution was immersed in a constant-temperature bath. The bath temperature was controlled within ± 0.2 K of the temperature range using a circulator temperature controller (HAAKE DC 50). Once the solution reached the desired temperature, it was weighed to within ± 0.0001 g with an analytical balance (AND GR-200). The uncertainty in the measurement of temperature was ± 0.1 K. Each reported density data was the average of three measurements. The experimental uncertainty in the measured density was estimated to be ± 4.8 × 10^{-4} g·cm^{-3}

Viscosity. The viscosity was measured using an Ostwald viscometer. The viscometer was immersed in a thermostated bath. The bath temperature was controlled within ± 0.2 K of the desired level using a circulator temperature controller (HAAKE DC 50). The uncertainty in the measurement of temperature was ± 0.1 K. Each reported value was the average of three measurements. The experimental uncertainty was estimated to be ± 0.005 mPa·s.

Results and Discussion

Density. To validate the pycnometer and the experimental procedure of the measurement, the densities of pure MDEA and mass fractions of 10 %, 20 %, and 30 % MDEA aqueous solutions were measured at (288, 313, and 333) K and compared with the values reported by Al-Ghawas et al.[15] and Maham et al.[16] These are presented in Table 1. The average absolute deviations of the density measurements are 0.15 %, 0.05 %, 0.07 %, and 0.13 % for pure MDEA and mass fractions of 10 %, 20 %, and 30 % MDEA aqueous solutions, respectively. Thus, the density data obtained in this study are in good

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Table 1. Comparison of the Densities, ρ, of Pure MDEA and of MDEA (1) + H_2O (2) Measured in This Work with Literature Values

	ρ/g·cm^{-3}											
	pure MDEA			$w_1 = 10$ %			$w_1 = 20$ %			$w_1 = 30$ %		
T/K	ref 15	ref 16	this work	ref 15	ref 16	this work	ref 15	ref 16	this work	ref 15	ref 16	this work
288	1.0445		1.0441	1.0078		1.0079	1.0180		1.0167	1.0290		1.0307
313	1.0267	1.02445	1.0272	1.0007	1.00069	1.0004	1.0091	1.00860	1.0086	1.0180	1.01727	1.0193
333	1.0123	1.00900	1.0126	0.9912	0.99092	0.9902	0.9993	0.99798	0.9995	1.0069	1.00547	1.0071
100AAD			0.15			0.05			0.07			0.13

Table 2. Comparison of the Viscosities, η, of Pure MDEA and of MDEA (1) + H_2O (2) Measured in This Work with Literature Values

	η/mPa·s											
	pure MDEA			$w_1 = 10$ %			$w_1 = 20$ %			$w_1 = 30$ %		
T/K	ref 15	ref 17	this work	ref 15	ref 17	this work	ref 15	ref 17	this work	ref 15	ref 17	this work
288	141.9		142.0	1.707		1.703	2.650		2.624	4.402		4.399
313	34.78	34.11	34.73	0.907	0.902	0.899	1.301	1.260	1.305	1.937	1.893	1.929
333	14.50	14.30	14.66	0.627	0.624	0.630	0.858	0.838	0.860	1.207	1.128	1.218
100AAD			1.11			0.58			1.51			2.13

Table 3. Density, ρ, for PZ (1) + MDEA (2) + H_2O (3) and PZ (1) + AMP (2) + H_2O (3) from (288 to 333) K with $w_1 + w_2 = 0.30$'

	ρ/g·cm^{-3}									
w_1/w_2	*T*/K = 288	*T*/K = 293	*T*/K = 298	*T*/K = 303	*T*/K = 308	*T*/K = 313	*T*/K = 318	*T*/K = 323	*T*/K = 328	*T*/K = 333
					PZ/MDEA					
3/27	1.0262	1.0239	1.0218	1.0197	1.0173	1.0150	1.0123	1.0095	1.0064	1.0032
6/24	1.0267	1.0245	1.0225	1.0200	1.0177	1.0152	1.0126	1.0098	1.0066	1.0035
9/21	1.0271	1.0253	1.0229	1.0203	1.0179	1.0154	1.0128	1.0100	1.0068	1.0038
12/18	1.0281	1.0264	1.0239	1.0216	1.0185	1.0160	1.0131	1.0103	1.0072	1.0040
					PZ/AMP					
3/27	1.0034	1.0009	0.9990	0.9963	0.9932	0.9909	0.9872	0.9840	0.9809	0.9780
6/24	1.0054	1.0037	1.0016	0.9989	0.9959	0.9930	0.9900	0.9869	0.9832	0.9804
9/21	1.0076	1.0055	1.0039	1.0012	0.9983	0.9957	0.9928	0.9893	0.9861	0.9828
12/18	1.0092	1.0075	1.0049	1.0025	0.9999	0.9970	0.9941	0.9908	0.9873	0.9843

agreement with the data of Al-Ghawas et al.[15] and Maham et al.[16] The measured densities of solutions of (PZ (1) + MDEA (2) + H_2O (3)) and (PZ (1) + AMP (2) + H_2O (3)) are presented in Table 3. *w* is the mass fraction of individual amine present in the solution. As shown in Table 3, densities of the ternary mixtures decrease with increasing temperature and increasing mass fraction of PZ in the mixture.

The molar volume of the liquid mixtures is correlated using the following expression:

$$V_m = V_m^{12} + V_m^{23} + V_m^{13} \quad (1)$$

where

$$V_m^{jk}/\mathrm{cm}^3\cdot\mathrm{mol}^{-1} = x_j x_k \sum_{i=0}^{n} A_i (x_j - x_k)^i \quad (2)$$

where A_i are pair parameters and are assumed to be temperature dependent:

$$A_i = a + b(T/\mathrm{K}) + c(T/\mathrm{K})^2 \quad (3)$$

The molar volume of the liquid mixtures is calculated by

$$V_m = \frac{\sum x_i M_i}{\rho_m} \quad (4)$$

where M_i is the molar mass of pure component *i*, ρ_m is the measured liquid density, and x_i is the mole fraction of the pure component *i*.

A general set of temperature-dependent parameters has been developed using experimental data in the temperature range (288 to 333) K. For convenience, we have considered PZ as the first component, MDEA or AMP as the second component, and H_2O as the third component in the ternary mixtures. The determined parameters are presented in Tables 4 and 5.

Table 4. Parameters A_0, A_1, and A_2 of Equation 2 for PZ (1) + MDEA (2) + H_2O (3)[a]

		binary pair		
parameters		PZ + MDEA	MDEA + H_2O	PZ + H_2O
A_0	*a*	−93401.36	34963.82	13019.44
	b	629.4204	−234.4859	−86.32541
	c	−1.050666	0.391559	0.144670
A_1	*a*	−207848.7	−3285.235	84259.66
	b	1401.612	21.21317	−568.7606
	c	−2.338962	−0.035485	0.949105
A_2	*a*	25844.53	−48483.73	84440.92
	b	−174.2754	327.6001	−569.5475
	c	0.290828	−0.546740	0.950023

[a] 100AAD = 0.01; no. of data points = 40.

Table 5. Parameters A_0, A_1, and A_2 of Equation 2 for PZ (1) + AMP (2) + H_2O (3)[a]

		binary pair		
parameters		PZ + AMP	AMP + H_2O	PZ + H_2O
A_0	*a*	−20886.09	−28440.72	24248.76
	b	127.1076	176.6886	−147.3027
	c	−0.191286	−0.267907	0.222152
A_1	*a*	190750.1	34227.46	−13126.72
	b	−1171.766	−210.5396	80.12318
	c	1.771560	0.317954	−0.121321
A_2	*a*	−34556.63	84848.73	−53126.76
	b	212.3032	−522.1517	326.0247
	c	−0.320993	0.790580	−0.492191

[a] 100AAD = 0.02; no. of data points = 40.

Viscosity. To validate the viscometer and the experimental procedure of the measurement, the viscosities of pure MDEA and mass fractions of 10 %, 20 %, and 30 % MDEA aqueous

Table 6. Viscosity, η, for PZ (1) + MDEA (2) + H_2O (3) and PZ (1) + AMP (2) + H_2O (3) from (288 to 333) K with $w_1 + w_2 = 0.30$

	η/mPa·s									
w_1/w_2	T/K = 288	T/K = 293	T/K = 298	T/K = 303	T/K = 308	T/K = 313	T/K = 318	T/K = 323	T/K = 328	T/K = 333
					PZ/MDEA					
3/27	4.007	3.570	3.245	2.860	2.413	2.104	1.737	1.493	1.236	0.871
6/24	4.961	4.270	3.584	3.099	2.683	2.285	2.015	1.771	1.512	1.257
9/21	5.699	4.814	4.116	3.452	2.965	2.520	2.264	1.899	1.610	1.389
12/18	6.240	5.328	4.402	3.826	3.246	2.770	2.455	2.116	1.814	1.481
					PZ/AMP					
3/27	5.398	4.499	3.752	3.042	2.557	2.088	1.776	1.497	1.296	1.117
6/24	5.477	4.674	3.892	3.182	2.626	2.227	1.886	1.596	1.342	1.147
9/21	5.645	4.665	4.065	3.327	2.749	2.344	2.077	1.762	1.541	1.343
12/18	5.871	4.823	4.105	3.409	2.817	2.444	2.166	1.957	1.753	1.562

Table 7. Parameters G_{12}, G_{23}, and G_{13} of Equation 6 for PZ (1) + MDEA (2) + H_2O (3) and PZ (1) + AMP (2) + H_2O (3)

		ternary pairs	
parameters		PZ + MDEA + H_2O	PZ + AMP + H_2O
G_{12}	a	185839.8	−60176.18
	b	−1209.703	395.8351
	c	1.967817	−0.649916
G_{23}	a	−1267.816	449.6665
	b	8.859421	−2.407320
	c	−0.015248	0.003185
G_{13}	a	−5479.227	4076.037
	b	36.27614	−26.37798
	c	−0.059750	0.042811

solutions were measured at (288, 313, and 333) K and compared with the values reported by Al-Ghawas et al.[15] and Teng et al.[17] These are presented in Table 2. The average absolute deviations of the viscosity measurements are 1.11 %, 0.58 %, 1.51 %, and 2.13 % for pure MDEA and mass fractions of 10 %, 20 %, and 30 % MDEA aqueous solutions, respectively. Thus, the viscosity obtained in this study are in good agreement with the data of Al-Ghawas et al.[15] and Teng et al.[17] The measured viscosities of solution of (PZ(1) + MDEA (2) + H_2O (3)) and (PZ (1) + AMP (2) + H_2O (3)) are presented in Table 6. According to Table 6, viscosities of the ternary mixtures decrease with increasing temperature and decreasing mass fraction of PZ in the mixture.

The viscosities of the liquid mixtures are correlated using the following expression:

$$\ln(\eta_m/\text{mPa·s}) = \sum\sum x_i x_j G_{ij} \quad (5)$$

where x_i is the mole fraction of the ith component in the mixture. For a ternary system

$$\ln(\eta_m/\text{mPa·s}) = x_1x_2G_{12} + x_2x_3G_{23} + x_1x_3G_{13} \quad (6)$$

G_{ij} in eq 5 are temperature-dependent and are assumed to have the form

$$G_{ij} = a + b(T/\text{K}) + c(T/\text{K})^2 \quad (7)$$

The parameters of eq 5 are obtained by regression analysis of the experimental data of this work and are presented in Table 7. The calculated viscosities from the correlation (eq 5) are excellent agreement with the experimental data, the average absolute deviation between the correlated and the experimental data for the (PZ + MDEA + H_2O) and (PZ + AMP + H_2O) systems being about 1.8 %, and 1.2 %, respectively.

Conclusion

The densities and viscosities of four (MDEA + PZ + H_2O) and (AMP + PZ + H_2O) mixtures were measured and correlated over the temperature range (288 to 333) K. The correlated densities and viscosities of the binary and ternary mixtures are in excellent agreement with the experimental data over the temperature and relative composition ranges studied.

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