

Density and Viscosity of Aqueous Solutions of (2-Piperidineethanol + Piperazine) from (288 to 333) K and Surface Tension of Aqueous Solutions of (*N*-Methyldiethanolamine + Piperazine), (2-Amino-2-methyl-1-propanol + Piperazine), and (2-Piperidineethanol + Piperazine) from (293 to 323) K

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The densities and viscosities of aqueous blends of 2-piperidineethanol (2-PE) with piperazine (PZ) at (288, 293, 298, 303, 308, 313, 318, 323, 328, and 333) K as well as the surface tension of aqueous blends of PZ with *N*-methyldiethanolamine, 2-amino-2-methyl-1-propanol, and 2-PE at (293, 298, 303, 308, 313, 318, and 323) K have been measured. The total amine mass fraction in all solutions was kept within 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 acid gases such as CO₂ and H₂S from industrial gas streams by absorption into aqueous alkanolamine solvents is usually employed in industry. 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 CO₂, which leads to lower energy requirement for regeneration. Sterically hindered amines, such as, 2-amino-2-methyl-1-propanol (AMP) and 2-piperidineethanol (2-PE), have been shown to have higher absorption capacity, absorption rate, selectivity, and degradation resistance advantages over conventional amines such as monoethanolamine (MEA), diethanolamine (DEA), and *N*-methyldiethanolamine (MDEA).^{2,3} 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 CO₂.^{4–6} The rate constant of PZ has been found to be 1 order higher than that of conventional alkanolamines such as MEA.⁷ The physical properties (for example, density, viscosity, and surface tension of aqueous amine solutions) are essential for the rational design of gas treating units and for optimum gas treating processes. Surface tension of aqueous amine solutions is also very important for the separation of acid gases using microporous membranes as a gas–liquid contactor.⁸

In our previous work, the densities and viscosities were presented for aqueous solutions of 2-PE, (2-PE + MEA), (2-PE + DEA), (MDEA + PZ), and (AMP + PZ).^{9,10} In this work, the density and viscosity of aqueous solutions of (2-PE + PZ) were measured over the temperature range (288 to 333) K, and the surface tension of aqueous solutions of (MDEA + PZ), (AMP + PZ), and (2-PE + PZ) were measured over the temperature range (293 to 323) K. The total amine mass fraction in the solution was kept within 30 %. The density and viscosity of the ternary mixtures are correlated as a function of temperature and amine concentration.

Experimental Section

Materials. Reagent grade 2-PE of 95 % purity was obtained from Acros Organic, and 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 solution was estimated as ± 0.007 %.

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). The desired temperature of the amine solutions was checked with Pt 100 temperature sensor. 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 $\pm 3.7 \times 10^{-4}$ g·m⁻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.

Surface Tension. The surface tension measurement was carried out with a GBX tensiometer (model ILMS-4), using the Du Noüy ring method. The temperature was controlled within ± 0.2 K of the desired level using a circulator temperature controller (Julabo F 12). 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 ± 0.12 mN·m⁻¹.

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Table 1. Comparison of the Densities, ρ , of Pure MDEA and of MDEA (1) + H₂O (2) Measured in This Work with Literature Values

T K	$\rho/\text{g}\cdot\text{cm}^{-3}$											
	pure MDEA			$w_1 = 10\%$			$w_1 = 20\%$			$w_1 = 30\%$		
	ref 11	ref 12	this work	ref 11	ref 12	this work	ref 11	ref 12	this work	ref 11	ref 12	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) + H₂O (2) Measured in This Work with Literature Values

T K	$\eta/\text{mPa}\cdot\text{s}$											
	pure MDEA			$w_1 = 10\%$			$w_1 = 20\%$			$w_1 = 30\%$		
	ref 11	ref 13	this work	ref 11	ref 13	this work	ref 11	ref 13	this work	ref 11	ref 13	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. Comparison of the Surface Tension, γ , of Aqueous MDEA Solutions Measured in This Work with Literature Values

T K	$\gamma/\text{mN}\cdot\text{m}^{-1}$											
	10% MDEA				20% MDEA				30% MDEA			
	refs 14 and 15		this work		refs 14 and 15		this work		refs 14 and 15		this work	
293	62.24		62.35		58.47		58.41		55.27		55.14	
313	58.08		57.91		54.56		54.71		51.47		51.37	
323	55.68		55.89		52.73		52.59		50.17		50.21	
100AAD			0.28				0.21				0.17	

Table 4. Density, ρ , for PZ (1) + 2-PE (2) + H₂O (3) from (288 to 333) K with $w_1 + w_2 = 0.30$

w_1/w_2	$\rho/\text{g}\cdot\text{cm}^{-3}$									
	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
3/27	1.0188	1.0157	1.0139	1.0103	1.0075	1.0041	1.0015	0.9985	0.9953	0.9922
6/24	1.0198	1.0169	1.0147	1.0111	1.0085	1.0053	1.0026	0.9992	0.9961	0.9933
9/21	1.0209	1.0181	1.0158	1.0125	1.0095	1.0064	1.0039	1.0009	0.9975	0.9943
12/18	1.0218	1.0192	1.0169	1.0133	1.0107	1.0077	1.0047	1.0017	0.9981	0.9958

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.¹¹ and Maham et al.¹² 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 agreement with the data of Al-Ghawas et al.¹¹ and Maham et al.¹² The measured densities of the solutions of (PZ (1) + 2-PE (2) + H₂O (3)) are presented in Table 4. w is the mass fraction of individual amine present in the solution.

The molar volume of the liquid mixtures is correlated using the following expression:¹⁰

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

where

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

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

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

Table 5. Parameters A_0 , A_1 , and A_2 of the Equation $V_m^{jk}/\text{cm}^3\cdot\text{mol}^{-1} = x_j x_k \sum_{i=0}^n A_i (x_j - x_k)^i$ for PZ (1) + 2-PE (2) + H₂O (3)^a

parameters	binary pair			
	PZ + 2-PE	2-PE + H ₂ O	PZ + H ₂ O	
A_0	a	132501.5	-34477.40	-27817.59
	b	-844.4391	220.8569	178.8769
	c	1.332153	-0.348236	-0.282080
A_1	a	248103.2	1086.310	-125086.8
	b	-1580.181	-7.856972	796.1994
	c	2.492814	0.012235	-1.256149
A_2	a	-28644.15	45639.09	-111482.5
	b	182.4417	-290.0138	709.5963
	c	-0.287811	0.457656	-1.119321

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

$$100\text{AAD} = \frac{1}{N} \sum_{i=1}^N \frac{|\rho_{\text{expt},i} - \rho_{\text{calcd},i}|}{\rho_{\text{expt},i}}$$

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, 2-PE as the second component, and H₂O as third component in the ternary mixtures. The determined parameters are presented in Table 5. The comparisons between the measured and correlated densities are shown in Figure 1. As shown in this figure, densities of the ternary mixtures increase with

Table 6. Viscosity, η , for PZ (1) + 2-PE (2) + H₂O (3) from (288 to 333) K with $w_1 + w_2 = 0.30$

w_1/w_2	$\eta/\text{mPa}\cdot\text{s}$									
	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
3/27	5.334	4.771	3.941	3.508	3.123	2.563	2.325	1.985	1.851	1.601
6/24	5.890	4.912	4.171	3.597	3.269	2.742	2.388	2.141	1.932	1.654
9/21	6.457	5.270	4.619	3.950	3.332	2.951	2.643	2.249	2.017	1.714
12/18	7.200	5.810	5.146	4.316	3.812	3.351	2.919	2.381	2.029	1.795

Table 7. Parameters G_{12} , G_{23} , and G_{13} of the Equation $\ln(\eta_m/\text{mPa}\cdot\text{s}) = x_1x_2G_{12} + x_2x_3G_{23} + x_1x_3G_{13}$ for PZ (1) + 2-PE (2) + H₂O (3)^a

parameters	ternary pairs	
	PZ + 2-PE + H ₂ O	
G_{12}	a	62640.73
	b	-412.6692
	c	0.675724
G_{23}	a	144.4600
	b	-0.293910
	c	-0.351325×10^{-3}
G_{13}	a	-2047.386
	b	14.11455
	c	-0.023873

^a 100AAD = 1.67; no. of data points = 40.

$$100\text{AAD} = \frac{1}{N} \sum_{i=1}^N \frac{|\eta_{\text{expt},i} - \eta_{\text{calcd},i}|}{\eta_{\text{expt},i}}$$

decreasing temperature and increasing mass fraction of PZ in the mixture.

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 solutions were measured at (288, 313, and 333) K and compared with the values reported by Al-Ghawas et al.¹¹ and Teng et al.¹³ 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.¹¹ and Teng et al.¹³ The measured viscosities of solution of (PZ(1) + 2-PE (2) + H₂O (3)) are presented in Table 6. w is the mass fraction of individual amine present in the solution.

The viscosities of the liquid mixtures are correlated using the following expression:¹⁰

$$\ln(\eta_m/\text{mPa}\cdot\text{s}) = \sum_{i=1}^n \sum_{j>i}^n x_i x_j G_{ij} \quad (5)$$

Table 8. Surface Tension, γ , for PZ (1) + MDEA (2) + H₂O (3) from (293 to 323) K with $w_1 + w_2 = 0.30$

w_1/w_2	$\gamma/\text{mN}\cdot\text{m}^{-1}$						
	T/K = 293	T/K = 298	T/K = 303	T/K = 308	T/K = 313	T/K = 318	T/K = 323
3/27	55.66	54.86	54.14	53.05	52.43	51.26	50.78
6/24	55.89	55.04	54.74	53.28	52.80	51.99	51.14
9/21	56.42	55.57	55.05	54.25	53.33	52.43	51.85
12/18	56.88	55.83	55.28	54.73	54.03	53.13	52.45

Table 9. Surface Tension, γ , for PZ (1) + AMP (2) + H₂O (3) from (293 to 323) K with $w_1 + w_2 = 0.30$

w_1/w_2	$\gamma/\text{mN}\cdot\text{m}^{-1}$						
	T/K = 293	T/K = 298	T/K = 303	T/K = 308	T/K = 313	T/K = 318	T/K = 323
3/27	48.13	47.28	46.36	45.31	44.62	43.34	42.13
6/24	48.85	47.91	46.88	46.06	45.28	44.21	43.22
9/21	49.01	48.14	47.22	46.22	45.44	44.29	43.59
12/18	49.37	48.51	47.60	46.70	45.93	44.89	43.90

Table 10. Surface Tension, γ , for PZ (1) + 2-PE (2) + H₂O (3) from (293 to 323) K with $w_1 + w_2 = 0.30$

w_1/w_2	$\gamma/\text{mN}\cdot\text{m}^{-1}$						
	T/K = 293	T/K = 298	T/K = 303	T/K = 308	T/K = 313	T/K = 318	T/K = 323
3/27	43.72	43.11	42.20	41.32	40.79	40.43	39.73
6/24	44.17	43.31	42.58	42.05	41.22	40.55	39.97
9/21	44.37	43.43	42.77	42.22	41.45	40.72	40.27
12/18	44.53	43.63	42.92	42.42	41.76	40.92	40.48

where x_i is the mole fraction of the i th component in the mixture.

For a ternary system

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

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

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

The parameters of eq 6 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 6) are excellent agreement with the experimental data, the average absolute deviation between the correlated and the experimental data being about 1.67 %. The comparisons between the measured and correlated viscosities are shown in Figure 2. As shown in this figure, viscosities of the ternary mixtures increase with decreasing temperature and increasing mass fraction of PZ in the mixture.

Surface Tension. To validate the tensiometer and the experimental procedure of the measurement, the surface tension of mass fractions of (10, 20, and 30) % MDEA aqueous solutions were measured at (293, 313, and 323) K and compared with the values reported by Rinker et al.¹⁴ and Aguila-Hernández et al.¹⁵ These are presented in Table 3. The average absolute deviations for the surface tension measurements are (0.28, 0.21, and 0.17) % for mass fractions of (10, 20, and 30) % MDEA aqueous solutions, respectively. Thus, the surface tension obtained in this study are in good agreement with the data of Rinker et al.¹⁴ and Aguila-Hernández et al.¹⁵ The measured surface tension of solution of (PZ(1) + MDEA (2) + H₂O (3)),

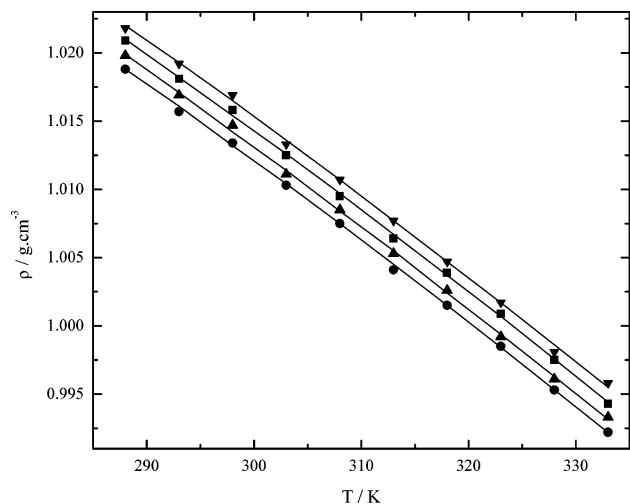


Figure 1. Density of PZ (1) + 2-PE (2) + H₂O (3) system at various temperatures: ●, $w_1/w_2 = 3/27$; ▲, $w_1/w_2 = 6/24$; ■, $w_1/w_2 = 9/21$; ▼, $w_1/w_2 = 12/18$. Lines are calculated by eq 2.

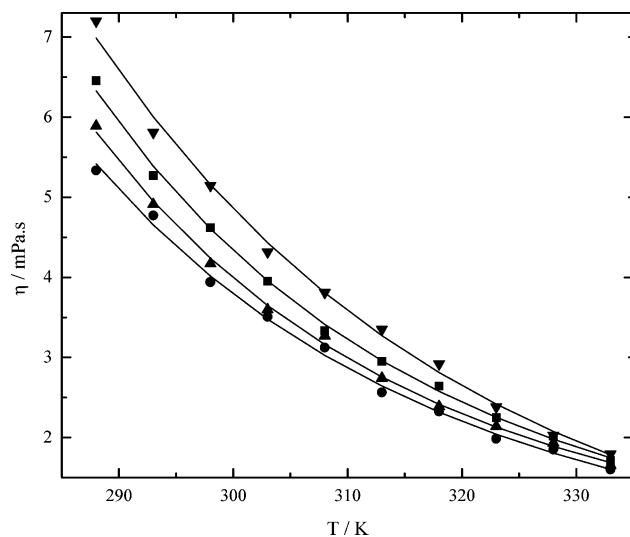


Figure 2. Viscosity of PZ (1) + 2-PE (2) + H₂O (3) system at various temperatures: ●, $w_1/w_2 = 3/27$; ▲, $w_1/w_2 = 6/24$; ■, $w_1/w_2 = 9/21$; ▼, $w_1/w_2 = 12/18$. Lines are calculated by eq 6.

(PZ(1) + AMP (2) + H₂O (3)), and (PZ(1) + 2-PE (2) + H₂O (3)) are presented in Tables 8 to 10. w is the mass fraction of individual amine present in the solution. Surface tension of the ternary mixtures decrease with increasing temperature and decreasing mass fraction of PZ in the mixture. There is small variation in surface tension with the changes of individual amine mass fractions.

Conclusions

The densities and viscosities of four (2-PE + PZ + H₂O) mixtures were measured and correlated over the temperature

range (288 to 333) K, and the surface tension of four (MDEA + PZ + H₂O), (AMP + PZ + H₂O) and (2-PE + PZ + H₂O) mixtures were measured over the temperature range (293 to 323) K. The correlated densities and viscosities are in excellent agreement with the experimental data over the temperature and relative composition ranges studied.

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