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SHORT ARTICLE

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Physical Properties of Aqueous Solutions of Piperazine and (2-Amino-2-methyl-1-propanol + Piperazine) from (298.15 to 333.15) K

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ABSTRACT: The density (ρ), viscosity (η), surface tension (σ), and refractive index (n_D) of aqueous solutions of piperazine and aqueous blends of 2-amino-2-methyl-1-propanol (AMP) with piperazine were experimentally measured for a wide range of temperature (298.15 to 333.15) K. The physical properties were measured for piperazine mass fractions (1.74, 3.45, 6.88, and 10.35) and for aqueous blends of (AMP + PZ) with mass fractions {100 (w_1/w_2) = (28.26/1.74), (26.55/3.45), (23.12/6.88), (19.65/10.35)}. The concentrations for aqueous solutions of (AMP + PZ) were kept higher due to the growing interest in use of concentrated amines in gas processing. All of the measured physical property values were correlated as a function of temperature.

INTRODUCTION

Alkanolamines are being used for the removal of acid gases such as carbon dioxide (CO_2) and hydrogen sulphide (H_2S) from the process of different industrial gaseous streams through the absorption process. The most industrially used alkanolamines include monoethanolamine (MEA), diethanolamine (DEA), *N*-methyldiethanolamine (MDEA), and 2-amino-2-methyl-1-propanol (AMP).[1] AMP belongs to a new class of amines which is called sterically hindered amines. This hindrance is caused by the presence of bulky group adjacent to the amino group. Sterically hindered amine (AMP) is the potential absorbent for CO_2 removal with relatively high CO_2 loading, selectivity, and efficient regeneration due to unstable carbamate formation.[2,3] To get the higher CO_2 removal and low regeneration energy and to cope with economic and environmental limitations, the blends of primary and tertiary amines or secondary and tertiary amines are suggested.[4,5] These blends combine the properties of higher absorption capacity of tertiary amines with a higher reaction rate of secondary or primary amines, and therefore a high removal of acid gases can be achieved.[6] The use of an activator is also getting significant attraction to enhance the absorption capacity and rate of reaction. Piperazine (PZ) is being used as an activator for CO_2 removal. Piperazine activated aqueous AMP system for CO_2 removal has been studied by researchers in the recent times.[7,8] The kinetic study shows that the introduction of small amount of piperazine (PZ) to the aqueous solution of AMP significantly increases the rate of absorption.[9,10] Therefore, the piperazine activated AMP solution could be one of the potential solvent for the bulk removal of CO_2 from the gaseous streams with industrial interest.

The knowledge of physical properties such as density, viscosity, surface tension, and refractive index is essential to design the absorption system for acid gas removal. The properties such as density and viscosity are important to design the acid gas contactor, rate modeling, and reaction rate constants.[11−13] Surface tension is important in designing of liquid gas absorber as it affects the column hydrodynamics, mass transfer, and gas hold up.[14,15] Refractive index values provide a satisfactory analytical method to determine the composition of solvents. These values are used to calculate molar refractions which can be used to further understand molecular interactions in the mixtures.[16−18] The available literature for physical properties of PZ is scarce and limited in certain compositions and temperatures. However, the literature review for the determination of physical properties of (AMP + PZ) revealed that available physical properties are limited and inconsistent.[1,5,14,18] Therefore, new experimental data for physical properties (density, viscosity, surface tension, and refractive index) of PZ and (AMP + PZ) for wide range of temperature and compositions are presented. The measured physical properties are correlated as a function of temperature.

EXPERIMENTAL SECTION

Materials. Piperazine with a purity of 99.9 % (GC, area %) and AMP 95 % (GC area %) were purchased from Merck, Malaysia and were used without further purification. The bidistilled water was used to prepare solutions. All of the solutions were prepared gravimetrically using an analytical balance (Mettler Toledo AS120S) with a measuring accuracy of ± 0.0001 g. The total amine concentrations were also experimentally determined by titration with 0.5 M HCl using methyl orange indicator, and the concentrations were accurate within ± 0.1 %.

Density. A digital vibrating glass U-tube densitometer (DMA 5000, Anton Paar) with the measuring accuracy of $\pm 1.0 \cdot 10^{-5}$ g·cm^{-3} was used to measure the density of binary solutions of AMP. The density meter was calibrated before each measurement with water of Millipore quality. All of the densities were measured at a temperature range of (298.15 to 333.15) K with a temperature controlled accuracy of ± 0.01 K (PT 100). The experimental uncertainty of measured density at corresponding temperature was estimated to be as $\pm 3 \cdot 10^{-5}$ g·cm^{-3} and ± 0.02 K, respectively.

Viscosity. Kinematic viscosities were measured using calibrated Ubbelohde viscometers of appropriate sizes. The viscometers were

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Table 1. Densities of (ρ/g·cm^{-3}) of Piperazine (2) + Water (3)

	100 (w_2)					
T/K	1.74	ref 19	3.45	6.88	10.35	ref 19
298.15	0.99775	0.998287	0.99852	1.00018	1.00223	1.001285
303.15	0.99637		0.99708	0.99869	1.00064	
308.15	0.99474	0.995233	0.99543	0.99697	0.99884	0.998022
313.15	0.99291		0.99359	0.99507	0.99686	
318.15	0.99090	0.991382	0.99156	0.99299	0.99473	0.993991
323.15	0.98872		0.98935	0.99074	0.99239	
328.15	0.98637		0.98698	0.98833	0.98992	
333.15	0.98383		0.98446	0.98577	0.98730	

Table 2. Viscosities (η/mPa·s) of Piperazine (2) + Water (3)

	(100 w_2)					
T/K	1.74	ref 19	3.45	6.88	10.35	ref 19
298.15	0.87	0.86	0.94	1.08	1.29	1.28
303.15	0.78		0.85	0.96	1.18	
308.15	0.71		0.75	0.86	1.04	
313.15	0.68	0.69	0.69	0.78	0.90	
318.15	0.59		0.63	0.71	0.84	
323.15	0.54		0.57	0.65	0.78	0.81
328.15	0.50		0.52	0.58	0.68	
333.15	0.46	0.47	0.48	0.54	0.62	0.59

Table 3. Surface Tension (σ/mN·m^{-1}) of Piperazine (2) + Water (3)

	(100 w_2)					
T/K	1.74	ref 19	3.45	6.88	10.35	ref 19
298.15	70.97		69.95	69.83	69.41	
303.15	70.09	71.48	69.18	68.99	68.37	69.1
313.15	69.11	69.34	68.21	68.11	67.44	67.92
323.15	67.93	67.84	67.29	67.06	66.45	65.37
333.15	66.99		66.48	66.14	65.31	

immersed in a thermostatic bath (Tamson, TVB445) with temperature controlled accuracy of ± 0.02 K. The sample was immersed for at least 15 min to get equilibrate with the set point before any measurement.[12] The efflux time was then measured using a manual stop watch with an accuracy of ± 0.01 s. The dynamic viscosity of samples was calculated by multiplying the corresponding density with kinematic viscosities. The uncertainty of the measured experimental viscosities at corresponding temperature was found to be as ± 0.05 mPa·s and ± 0.02 K, respectively.

Surface Tension. The surface tension of the binary and ternary solutions was measured using IFT 700 (VINCI Technologies) with a precision of ± 0.03 mN·m^{-1} with the temperature accuracy of ± 0.2 K. The pendent drop method was used to measure the surface tension in which a drop is created inside a thermostatic chamber, and a camera is installed which focuses and records the shape and contact angle properties. All of the values were measured between the temperature range of (298.15 to 333.15) K, and the reported data is the average of five data points. The measured experimental uncertainties at a corresponding temperature were found to be ± 0.04 mN·m^{-1} and ± 0.2 K.

Table 4. Refractive Indices (n_D) of Piperazine (2) + Water (3)

	(100 w_1)					
T/K	1.74	ref 19	3.45	6.88	10.35	ref 19
298.15	1.33796		1.34183	1.34759	1.35307	
303.15	1.33706	1.33449	1.34024	1.34608	1.35203	1.34847
313.15	1.33604	1.33366	1.33892	1.34482	1.35071	1.34797
323.15	1.33476		1.33759	1.34336	1.34957	
333.15	1.33348		1.33577	1.34221	1.34829	

Refractive Index. The refractive index of the binary and ternary solutions was measured using a digital refractometer (Atago, RX-5000 alpha) with a measuring accuracy of ± 4·10^{-5}. Experimentally measured values of refractive index cover the temperature range from (298.15 to 333.15) K with a temperature control accuracy of ± 0.05 K. The refractometer was calibrated for each set of experiments with Millipore water and checked with pure liquids of known refractive indices. The reported values are the average of five data points. The measured experimental uncertainties at a given temperature were found ± 5·10^{-5}.

RESULTS AND DISCUSSION

The experimentally measured physical properties (density, viscosity, surface tension, and refractive index) of binary solutions of piperazine (PZ) are presented in Tables 1 to 4 as a function of temperature and PZ mass fractions, respectively. The measured physical property values of binary solutions are compared with the work of Muhammad et al.[19] The average relative deviations of density, viscosity, surface tension, and refractive index measurements are (0.051, 0.083) %, (1.28, 3.45) %, (0.803, 1.138) %, and (0.19, 0.23) % for PZ mass fractions of 1.74 % and 10.35 %. The following eq 1 is used to calculated percent average relative deviations (% AAD).[20]

$$\%\text{AAD} = \frac{1}{n}\sum\left|\frac{X_{\text{exptl}} - Y_{\text{lit.}}}{Y_{\text{lit.}}}\right| \cdot 100 \qquad (1)$$

where n is the number of data points, X_{exptl} the measured physical property, and Y_{lit} physical property values from literature. All of the physical properties of binary solutions decrease with increasing temperature. Densities, viscosities, and refractive indices increase with increasing mass fractions of PZ in the solution. However, surface tension decreases with increasing both temperature and PZ mass fractions. The following eq 2 is used to correlate density, surface tension, and refractive indices as a function of temperature. The viscosity data are correlated as a function of temperature using eq 3.

$$Z = A_0 + A_1(T/\text{K}) \qquad (2)$$

$$\log(\eta) = A_0 + A_1/(T/\text{K}) \qquad (3)$$

where Z is density, surface tension, and refractive index, η is viscosity, A_0 and A_1 are the fitting parameters, and T is the

Table 5. Fitting Parameters A_0 and A_1 and SD of eqs 2 and 3 for Piperazine (1) + Water (2)

	A_0	A_1	SD	A_0	A_1	SD
		100 (w_1)				
		1.74			3.45	
ρ/g·cm^{-3}	1.12820	−0.00040	0.0111	1.13040	−0.00040	0.0126
η/mPa·s	−6.12	1778.39	0.01	−6.45	1904.21	0.01
σ/mN·m^{-1}	104.05	−0.11	0.11	98.74	−0.10	0.10
n_D	1.37500	−0.00010	0.008	1.38980	−0.00010	0.020
		6.88			10.35	
ρ/g·cm^{-3}	1.13550	−0.00050	0.0154	1.14240	−0.00050	0.0103
η/mPa·s	−6.51	1961.87	0.01	−6.75	2090.84	0.02
σ/mN·m^{-1}	100.24	−0.10	0.09	102.31	−0.11	0.16
n_D	1.39110	−0.00010	0.015	1.39230	−0.00010	0.010

Table 6. Densities of (ρ/g·cm^{-3}) 2-Amino-2-methyl-1-propanol (1) + Piperazine (2) + Water (3)

	100 (w_1/w_2)			
T/K	28.26/1.74	26.55/3.45	23.12/6.88	19.65/10.35
298.15	0.99815	0.99948	1.00229	1.00488
303.15	0.99537	0.99671	0.99954	1.00217
308.15	0.99246	0.99381	0.99666	0.99932
313.15	0.98944	0.99080	0.99366	0.99637
318.15	0.98631	0.98768	0.99056	0.99330
323.15	0.98308	0.98446	0.98735	0.99012
328.15	0.97975	0.98113	0.98404	0.98678
333.15	0.97631	0.97770	0.98062	0.98343

Table 7. Viscosities (η/mPa·s) of 2-Amino-2-methyl-1-propanol (1) + Piperazine (2) + Water (3)

	100 (w_1/w_2)			
T/K	28.26/1.74	26.55/3.45	23.12/6.88	19.65/10.35
298.15	3.24	3.33	3.46	4.12
303.15	2.74	2.75	2.89	3.68
308.15	2.31	2.33	2.42	3.25
313.15	1.96	2.01	2.07	2.89
318.15	1.65	1.75	1.80	2.55
323.15	1.42	1.51	1.57	2.19
328.15	1.29	1.35	1.36	1.88
333.15	1.16	1.18	1.23	1.61

temperature. The fitting parameters were calculated using the method of least-squares and presented in Table 5 along with standard deviations. The eq[19] 4 is used to calculate standard deviations of all of the measured physical properties.

$$SD = [\sum_{i}^{n} (Z_{expt} - Z_{calc})^2/n]^{1/2} \quad (4)$$

where SD represents standard deviations, Z_{expt} represents measured physical properties (density, viscosity, refractive index, surface tension), Z_{calc} represents calculated values, and n represents the total number of data points.

Table 8. Surface Tension (σ/mN·m^{-1}) of 2-Amino-2-methyl-1-propanol (1) + Piperazine (2) + Water (3)

	(100 w_1/w_2)			
T/K	28.26/1.74	26.55/3.45	23.12/6.88	19.65/10.35
298.15	45.39	46.02	46.69	47.83
303.15	44.15	44.66	45.32	46.29
313.15	42.72	43.26	43.82	44.42
323.15	41.06	41.52	42.09	42.77
333.15	39.72	40.14	40.71	41.14

Table 9. Refractive Indices (n_D) of 2-Amino-2-methyl-1-propanol (1) Piperazine (2) + Water (3)

	100 (w_1/w_2)			
T/K	28.26/1.74	26.55/3.45	23.12/6.88	19.65/10.35
298.15	1.37829	1.37895	1.38032	1.38156
303.15	1.37685	1.37763	1.37888	1.38024
313.15	1.37523	1.37615	1.37719	1.37891
323.15	1.37348	1.37443	1.37579	1.37749
333.15	1.37189	1.37306	1.37421	1.37601

The measured densities, viscosities, surface tension, and refractive index of ternary solutions of AMP (1) + PZ (2) + water (3) are presented in Tables 6 to 9, respectively, as a function of temperature and (AMP + PZ) mass fractions. All of the physical properties were investigated for the temperatures ranging from (298.15 to 333.15) K. The measured densities, viscosities ,and refractive indices of ternary solutions increase with decreasing temperature and increasing PZ mass fraction in the solutions. Equation 2 is used to correlate density and refractive index, and eq 3 is fit to viscosity data as a function of temperature. Fitting parameters of eqs 2 and 3 along with the SD are presented in Table 10. The surface tension values are correlated as a function of temperature by eq 2. The standard deviations (SD) and fitting parameters are tabulated in Table 10.

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Table 10. Fitting Parameters A_0 and A_1 and SD of eqs 2 and 3 for 2-Amino-2-methyl-1-propanol (1) + Piperazine (2) + Water (3)

	100 (w_1/w_2)					
	28.26/1.74			26.55/3.45		
ρ/g·cm^{-3}	1.18470	−0.00060	0.0088	1.18560	−0.00060	0.0083
η/mPa·s	−8.84	2981.21	0.02	−8.55	2900.61	0.01
σ/mN·m^{-1}	92.56	−0.16	0.15	94.65	−0.16	0.15
n_D	1.43110	−0.00020	0.007	1.42790	−0.00020	0.011
	23.12/6.88			19.65/10.35		
ρ/g·cm^{-3}	1.18740	−0.00060	0.0073	1.18830	−0.00060	0.0056
η/mPa·s	−8.69	2953.97	0.01	−7.44	2653.53	0.03
σ/mN·m^{-1}	96.24	−0.17	0.20	102.84	−0.19	0.22
n_D	1.43010	−0.00020	0.010	1.42670	−0.00020	0.015

It can be observed from Table 8 that the surface tension decreases with increasing temperature. However, there has been a slight increase in surface tension of ternary mixtures with the addition of PZ mass fractions to the aqueous solutions of AMP, but the increase is not significant, and this is in line with the findings of literature.[21]

CONCLUSION

Physical properties such as density, viscosity, refractive index, and surface tension of binary solutions of PZ and ternary solutions of (AMP + PZ) were experimentally measured over the entire range of temperature from (298.15 to 333.15) K. The measured and correlated values are found to be in good agreement. All of the physical properties have shown the decreasing effect while increasing the temperature. In ternary systems of (AMP + PZ), density, viscosity, refractive index, and surface tension increase while increasing PZ mass fraction in the solutions.

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