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Physical Properties of Piperazine (PZ) Activated Aqueous Solutions of 2-Amino-2-hydroxymethyl-1,3-propanediol (AHPD + PZ)

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ABSTRACT: Physical properties such as density, viscosity, surface tension, and refractive index of piperazine (PZ) activated aqueous solutions of 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD) were measured. The experiments covered the PZ mass fraction of (1.74 to 10.35) mass %. The AHPD concentration was varied from (13 to 25) mass %. These properties were investigated over the temperature range of (303.15 to 333.15) K and were correlated as a function of temperature. There was a decrease in all measured properties with increasing temperature.

1. INTRODUCTION

Alkanolamines are used for the removal of acid gases such as carbon dioxide (CO_2) and hydrogen sulfide (H_2S) from the process of different industrial gaseous streams through absorption process. The most industrially used alkanolamines include monoethanolamine (MEA), diethanolamine (DEA), and *N*-methyldiethanolamine (MDEA).[1] Recently sterically hindered amines are proposed as potential new solvents for acid gas removal due to their unique cyclic structure, high CO_2 loading, and efficient regeneration.[2−9] One of the sterically hindered amines is 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD). Reaction kinetics and solubility data show that AHPD is a good potential solvent for acid gas removal.[10−12] Recently there has been a growing interest in the use of aqueous solutions of alkanolamines containing an activator to enhance the rate of reaction. Piperazine (PZ) has emerged as an effective activator.[13−16] PZ has shown good performance as an effective activator with MDEA and MEA due to the rapid carbamate formation with CO_2. PZ-activated MDEA technology is already used by BASF. The addition of PZ to aqueous solutions of AHPD has also shown good solubility and acceleration in the rate of reaction with CO_2.[17,18] Therefore PZ-activated aqueous solution of AHPD could be a potential solvent for acid gas removal. There has been a significant interest shown by researchers to determine the thermodynamic properties such as the density, viscosity, surface tension, and refractive index of these binary and ternary solutions. These properties are used to get information on intermolecular interactions and to design the acid gas absorption system.[7,10,18,19] Therefore in this paper the physical properties (density, viscosity, surface tension, and refractive index) of aqueous solutions (AHPD + PZ) are measured over the wide range of temperature (298.15 to 333.15) K. The experiments covered the commercially important concentration range of PZ mass % (1.74 to 10.35).[20] The AHPD mass fraction was varied from (13 to 25) mass %. All of the measured physical properties were correlated as a function of temperature.

2. EXPERIMENTAL SECTION

2.1. Materials and Methods. AHPD of reagent grade (99.99 %), PZ with a purity of ≥ 99 %, and MDEA with a purity of > 98 % were purchased from Merck, Malaysia. All chemicals were used without any further purification. The bidistilled water was used to prepare solutions. All solutions were prepared gravimetrically using an

Table 1. Comparison of Experimental Results of Pure MDEA and Water With Literature Data

	MDEA						
	density/g·cm^{-3}				viscosity/mPa·s		
T/K	this work	ref 22	ref 24	% AAD	this work	ref 8	% AAD
303.15	1.03458	1.03449		0.01	57.28		
313.15	1.02675	1.02699	1.02545	0.02,[22] 0.12[24]	34.41	34.73	0.92
	surface tension/mN·m^{-1}				refractive index/n_D		
T/K	this work	ref 21	ref 26	% AAD	this work	ref 21	% AAD
303.15	38.26	38.74	38.08	1.20,[21] 0.47[26]	1.46008	1.46532	0.35
313.15	37.19	37.48	37.25	0.77,[21] 0.16[26]	1.45988	1.46074	0.05

	Water					
	density/g·cm^{-3}			viscosity/mPa·s		
T/K	this work	ref 25	% AAD	this work	ref 25	% AAD
303.15	0.99572	0.9956	0.01	0.806	0.802	0.49
313.15	0.99228	0.9922	0.01	0.659	0.656	0.45
	surface tension/mN·m^{-1}			refractive index/n_D		
T/K	this work	ref 27	% AAD	this work	ref 28	% AAD
303.15	71.02	71.21	0.26	1.33221	1.33250	0.02
313.15	69.38	69.52	0.20	1.33048	1.33062	0.01

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Table 2. Density (ρ/g·cm^{-3}) of Aqueous AHPD (1) + PZ (2)

	(100 w_1/100 w_2)								
T/K	13/1.74	13/6.88	13/10.35	19/1.74	19/6.88	19/10.35	25/1.74	25/6.88	25/10.35
303.15	1.03037	1.03386	1.03494	1.04603	1.04933	1.05159	1.06338	1.06624	1.06880
308.15	1.02820	1.03149	1.03278	1.04405	1.04722	1.04938	1.06121	1.06406	1.06649
313.15	1.02617	1.02935	1.03056	1.04192	1.04496	1.04702	1.05897	1.06169	1.06402
318.15	1.02396	1.02707	1.02819	1.03963	1.04255	1.04455	1.05659	1.05919	1.06143
323.15	1.02161	1.02464	1.02568	1.03708	1.04002	1.04193	1.05407	1.05658	1.05871
328.15	1.01912	1.02207	1.02305	1.03382	1.03738	1.03920	1.05145	1.05385	1.05590
333.15	1.01688	1.01957	1.02048	1.03074	1.03460	1.03635	1.04886	1.05100	1.05298

Table 3. Viscosity (η/mPa·s) of Aqueous AHPD (1) + PZ (2)

	(100 w_1/100 w_2)								
T/K	13/1.74	13/6.88	13/10.35	19/1.74	19/6.88	19/10.35	25/1.74	25/6.88	25/10.35
303.15	1.72	1.88	2.04	2.19	2.38	2.64	2.95	3.36	3.58
308.15	1.58	1.72	1.91	2.02	2.24	2.45	2.71	3.16	3.41
313.15	1.44	1.59	1.77	1.85	2.09	2.27	2.48	2.95	3.24
318.15	1.33	1.45	1.64	1.71	1.94	2.11	2.28	2.73	3.09
323.15	1.22	1.32	1.52	1.57	1.80	1.94	2.08	2.56	2.95
333.15	1.12	1.21	1.42	1.44	1.67	1.78	1.89	2.39	2.78

Table 4. Refractive Index (n_D) of Aqueous AHPD (1) + PZ (2)

	(100 w_1/100 w_2)								
T/K	13/1.74	13/6.88	13/10.35	19/1.74	19/6.88	19/10.35	25/1.74	25/6.88	25/10.35
298.15	1.35802	1.36808	1.37399	1.36741	1.37547	1.37921	1.37727	1.38694	1.39411
303.15	1.35708	1.36694	1.37284	1.36675	1.37399	1.37841	1.37628	1.38601	1.39283
308.15	1.35629	1.36632	1.37198	1.36587	1.37295	1.37778	1.37568	1.38541	1.39201
313.15	1.35563	1.36569	1.37146	1.36556	1.37198	1.37748	1.37491	1.38456	1.39129
318.15	1.35477	1.36499	1.37066	1.36467	1.37083	1.37688	1.37398	1.38385	1.39028
323.15	1.35449	1.36445	1.36976	1.36429	1.36982	1.37636	1.37351	1.38315	1.38969
333.15	1.35344	1.36389	1.36904	1.36365	1.36921	1.37551	1.37237	1.38241	1.38857

analytical balance (Mettler Toledo AS120S) with a measuring accuracy of ± 0.0001 g.

2.2. Density. The densities of amine solutions were measured using a digital vibrating glass U-tube densitometer (Anton Paar, DMA 5000) with the measuring accuracy of $\pm 1.0 \cdot 10^{-5}$ g·cm^{-3}. All 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 reported densities were measured after achieving thermal equilibrium, and the equipment was set to slow mode for better accuracy. Each reported data point is an average of at least three data points. The experimental uncertainty of measured density at corresponding temperature was estimated to be ± 0.02 K and $\pm 3.0 \cdot 10^{-5}$ g·cm^{-3}, respectively.

2.3. Viscosity. The kinematic viscosity was measured using calibrated Ubbelohde viscometers of appropriate sizes. Viscometers containing aqueous solutions were immersed in thermostatic bath (Tamson, TVB445) with a built-in stirring system. The bath temperature was regulated with a Pt100 temperature probe with a temperature-controlled accuracy of ± 0.01 K. The sample was immersed for at least 15 min to equilibrate with the set point before any measurement. The efflux time was then measured using a manual stop watch with an accuracy of ± 0.01 s. The kinematic viscosities were calculated by multiplying the efflux time with the viscometer constant with the following eq 1

$$v = Ct \tag{1}$$

where v is the kinematic viscosity, C is the viscometer constant, and t is the efflux time in seconds (s). The kinematic viscosities were reproducible within ± 1 %. The dynamic viscosities of aqueous solutions of (AHPD + PZ) were calculated by multiplying the corresponding densities with the measured kinematic viscosities.

2.4. Refractive Index. The refractive index of aqueous solutions was measured using a digital refractometer (Atago, RX-5000 alpha) with a measuring accuracy of $4.0 \cdot 10^{-5}$. The measured values of refractive index cover the temperature range from (303.15 to 333.15) K, and the temperature was controlled within ± 0.05 K. The reported values are the averages of five measurements. The measured experimental uncertainty at a given temperature was found to be $5.0 \cdot 10^{-5}$ and 0.05 K, respectively.

2.5. Surface Tension. The surface tension was measured by using IFT 700 (VINCI Technologies) with a precision of ± 0.03 mN·m^{-1} with the temperature accuracy of ± 0.2 K.

Table 5. Surface Tension (σ/mN·m^{-1}) of Aqueous AHPD (1) + PZ (2)

	(100 w_1/100 w_2)								
T/K	13/1.74	13/6.88	13/10.35	19/1.74	19/6.88	19/10.35	25/1.74	25/6.88	25/10.35
303.15	55.45	53.21	52.82	51.78	49.21	48.11	48.01	47.27	46.11
308.15	54.66	52.11	51.69	50.64	48.42	47.15	46.99	46.32	45.15
313.15	53.73	51.19	50.44	49.89	47.41	46.35	46.14	45.41	44.29
318.15	52.85	50.29	49.52	49.06	46.39	45.47	45.32	44.62	43.55
323.15	51.81	49.04	48.25	48.03	45.51	44.61	44.42	43.48	42.87
333.15	50.01	47.35	46.41	46.19	43.67	43.09	42.85	41.83	41.44

Table 6. Fitting Parameters A_o, A_1, and SD of Equation 3 and 4 for AHPD (1) + PZ (2) + Water (3)

	13/1.74			13/6.88			13/10.35		
	A_o	A_1	SD	A_o	A_1	SD	A_o	A_1	SD
ρ/g·cm^{-3}	1.1679	−0.0005	0.0147	1.1764	−0.0005	0.0093	1.1825	−0.0005	0.0043
η/mPa·s	−4.4933	1524.515	0.02	−4.5658	1574.5431	0.02	−3.5245	1282.6105	0.02
σ/mN·m^{-1}	105.1932	−0.1642	0.19	107.5475	−0.1799	0.25	108.1232	−0.1837	0.26
n_D	1.4005	−0.0001	0.01333	1.4102	−0.0001	0.01319	1.4208	−0.0002	0.0134
	19/1.74			19/6.88			19/10.35		
ρ/g·cm^{-3}	1.2008	−0.0005	0.0030	1.1987	−0.0005	0.0025	1.206	−0.0005	0.0029
η/mPa·s	−4.1293	1487.8865	0.02	−3.3101	1266.892	0.01	−3.526	1361.4385	0.01
σ/mN·m^{-1}	108.6855	−0.1884	0.28	96.8118	−0.1576	0.26	94.2748	−0.1529	0.18
n_D	1.4077	−0.0001	0.01086	1.4300	−0.0002	0.00489	1.4102	−0.0001	0.0014
	25/1.74			25/6.88			25/10.35		
ρ/g·cm^{-3}	1.2113	−0.0005	0.0040	1.2209	−0.0005	0.0032	1.2292	−0.0005	0.0092
η/mPa·s	−4.0766	1562.2518	0.01	−2.8532	1232.0554	0.01	−1.7126	906.2955	0.01
σ/mN·m^{-1}	93.8462	−0.152	0.22	103.3463	−0.1853	0.24	94.2884	−0.1596	0.21
n_D	1.4184	−0.0001	0.01213	1.4245	−0.0001	0.0084	1.4397	−0.0002	0.01448

The pendant 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 values were measured between the temperature range of (298.15 to 333.15) K, and the reported data point is the average of five data points. The measured experimental uncertainties at a corresponding temperature were found to be $\pm$ 0.05 mN·m^{-1} and $\pm$ 0.3 K.

3. RESULTS AND DISCUSSION

All equipment used to measure the physical properties such as the density, viscosity, surface tension, and refractive index was calibrated. The calibration was made with water of Millipore quality and with pure liquids (MDEA) of known properties, and a comparison was made with the literature.[21,22,24−28] There is a good agreement found between literature and the present work as indicated by the percent average absolute deviation (% AAD) values presented in Table 1. The percent average absolute deviation (% AAD) presented in Table 1 was calculated by the following equation[23]

$$\%\text{AAD} = \frac{1}{n}\sum\left|\frac{X_{\text{exptl}} - Y_{\text{lit}}}{Y_{\text{lit}}}\right|\cdot 100 \qquad (2)$$

The measured values of density, viscosity, surface tension, and refractive index of aqueous (AHPD + PZ) are presented in Tables 2 to 5 as a function of temperature and concentration, where w_1 and w_2 represent the mass fractions of AHPD and PZ respectively. All measurements were made over a wide range of temperature ranging from (303.15 to 333.15) K. The density and refractive index values decrease linearly with increasing temperature and increase by increasing PZ concentrations in aqueous AHPD. However, surface tension values decrease linearly by increasing both temperature and mass fractions of PZ and AHPD. The density and refractive index surface tension data were fit to the following equation

$$Z = A_0 + A_1 T \qquad (3)$$

Viscosity values increase with the increase of PZ concentration in aqueous solutions of AHPD, or in other words viscosity increases by increasing the AHPD/PZ ratio as shown in Table 3. The viscosity values show a nonlinear decreasing trend, while increasing temperature and therefore viscosity data was fit to the following logarithmic equation

$$\log(\eta) = A_o + A_1/T \qquad (4)$$

where Z = (density, refractive index, and surface tension), η is viscosity, A_o and A_1 are fitting parameters, and T is the temperature in K. These parameters were calculated using the method of least-squares and presented in Table 6 along with the standard deviations. Equation 5 was used to calculate standard deviations[21]

$$SD = [\sum_{i}^{n} (Z_{exptl} - Z_{calcd})^2/n]^{1/2} \quad (5)$$

where SD represents standard deviations, Z_{exptl} represents measured physical properties, Z_{calcd} represents calculated values, and n represents the total number of data points.

4. CONCLUSION

Physical properties like the density, viscosity, and surface tension of aqueous solutions of (AHPD + PZ) were experimentally measured. The measurements were made over the temperature range of (298.15 to 333.15) K. An overall decrease in all properties was observed with increasing temperature. However, density, viscosity, and refractive index values increase by increasing the AHPD/PZ ratio, but the AHPD/PZ ratio shows an inverse effect on surface tension values. The empirical correlations were used to correlate all of the measured properties as a function of temperature.

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