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Thermophysical Analysis of Aqueous Solutions of Piperazine (PZ) and 2-Amino-2-hydroxymethyl-1, 3-propanediol + Piperazine (PZ + AHPD)

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Abstract

Physical properties such as density, viscosity, and surface tension of aqueous solutions of Piperazine (PZ) with mass fractions ($100\ w = 6.88, 13.76$) were measured. All these properties were also measured for aqueous blends of 2-amino-2-hydroxymethyl-1,3-propanediol with Piperazine (AHPD + PZ) with mass fractions { $100\ (w_1/w_2)$ = (1/6.88, 1/13.76, 7/6.88, 7/13.76, 13/6.88, 13/13.76 and 19/6.88, 19/13.76) }. These properties were investigated over the temperature range of 298.15 K to 333.15 K and were correlated as a function of temperature. There was a decrease in all measured properties with increasing temperature

Keywords: CO_2, AHPD, PZ, Acid Gas Contactor, Physical Properties

1. Introduction

Alkanolamines are used for the removal of acid gases such as carbon dioxide (CO2) and hydrogen sulphide (H2S) from the process of different industrial gaseous streams through absorption process. The most industrially used alkanolamines include; mono-ethanolamine (MEA), di-ethanolamine (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 CO2 loading and efficient regeneration .2-10 One of the sterically hindered amines is 2-Amino-2-hydroxymethyl-1,3-prpoanediol (AHPD). Reaction kinetics and solubility data shows that AHPD is a good potential solvent for acid gas removal.11-13 Recently there has been a growing interest in use of aqueous solutions of alkanolamines containing an activator to enhance the rate of reaction. Piperazine (PZ) has emerged as an effective activator.14-17 The addition of PZ to aqueous solution of AHPD has shown acceleration in the rate of reaction with CO2.18 Therefore, PZ activated aqueous solution of AHPD could be a potential solvent for acid gas removal. The knowledge of physical properties of solvents is essential to design the absorption system for acid gas removal. The properties like density and viscosity are also important for the determination of rate of reaction and mass transfer rate modeling of gas sweetening unit.7,11,19 Surface tension can also affect the important design parameters such as the column hydrodynamics and gas holdup in the acid gas contactor.20 Therefore, in this paper the physical properties (density, viscosity and surface tension) of aqueous solutions of PZ and (AHPD + PZ) are presented.

All the experimentally measured physical properties were also correlated as a function of temperature.

2. Materials and Methods

Piperazine with a purity of 99.9 % (GC, area %) an AHPD 99 % (GC area %) were purchased from Merck, Malaysia and were used without further purification. The bi-distilled water was used to prepare solutions. All the solutionswere 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 with in ± 0.1 %.

2.1 Density

The densities of aqueous solutions of PZ and (AMP + PZ) were measured using a digital vibrating glass U-tube densitometer (DMA 5000, Anton Paar) with the measuring accuracy of ± 0.000005 $g.m^{-3}$. The density meter was calibrated before and after each measurement with water of Millipore quality. All 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 reported densities were measured after achieving thermal equilibrium and the equipment was set to slow mode for better accuracy. Each reported data is the average of at least three data points. The experimental uncertainty of measured density was estimated ± 5. 10^{-6} g . cm^{-3}

2.2 Viscosity

The viscosities of aqueous solutions were measured using a calibrated Ubbelohde viscometer of sizes. The viscometer containing amine solutions was immersed in thermostatic bath (Tamson, TVB445) with built in stirring system with temperature controlled accuracy of ± 0.01 K. The bath temperature was regulated with Pt-100 temperature probe. The kinematic viscosities were calculated by multiplying the efflux time with the viscometer constant with the following 1

$$\upsilon = Ct \qquad (1)$$

Where υ is the kinematic viscosity in centistokes (cSt), C is the viscometer constant (cSt . s-1) and t is the efflux time in seconds (s). The dynamic viscosities of the aqueous amine solutions were calculated by multiplying the corresponding densities with the measured kinematic viscosities with an uncertainty of ± 0.028 mPa. S.

2.3 Surface Tension

The surface tension was measured using IFT 700 (VINCI Technologies) with a precision of ± 0.03 mN/m 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 the values were measured between the temperature range of (298.15 to 333.15) K and the reported data is the average of 5 data points. The measured experimental uncertainties at a corresponding temperature were found ± 0.38 mN . m-1 and ± 0.2 K

3 Results and Discussion

The density of aqueous solutions of PZ (2) and (AHPD (1) + PZ (2)) was measured over the temperature range of 298.15 K to 333.15 K. The measured values are presented in Table 1 as a function of temperature and concentration. Where w1 and w2 representing the mass fractions of AHPD and PZ respectively. The measured densities were correlated as a function of temperature by the following eq 2

$$Z = A_0 + A_1 T \qquad (2)$$

Where Z represents density or surface tension, A0, A1 are fitting parameters and T is the temperature in K. These parameters were calculated using the method of least square and presented in Table 2 along with the standard deviations. The eq 3 was used to calculate standard deviations

$$SD = \left[\sum_{i}^{n} (Z_{exptl} - Z_{calcd}) \; / \, n \right]^{1/2} \qquad (3)$$

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. The measured viscosities are presented in Table 3 as a function of temperatureand concentrations. The measurements were made for a temperature range from 298.15 K to 333.15 K. It is indicated from Table 3 that there is a decrease in viscosity values over the entire range of temperature. However an increasing trend in viscosity values of aqueous solutions of PZ (2) and (AHPD (1) + PZ (2)) systems was observed with the increase in concentration of PZ (2) and AHPD (1). The following eq 4 was used to correlate the measured viscosity values as a function of temperature

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

Where η is viscosity, Ao, A1 are fitting parameters and T is temperature in K. The fitting parameters and standard deviations are presented in Table 4 and eq 3 was used to calculate the standard deviations. Surface tension of aqueous solution of PZ (2) and (AHPD (1) + PZ (2)) was measured for the temperature range of (1) + PZ (2)) was measured for the temperature range of 298.15 K to 333.15 K. According to Table 5 the measured surface tension values decreased with increasing temperature. Surface tension also decreased as the concentration of both PZ and AHPD increased. The measured values were fitted to the eq 2 as a function of temperature and standard deviations were calculated by eq 3. The fitting parameters along with standard deviations are listed in Table 6

Table 1. Density ρ (g.m^{-3}) of Aqueous PZ (2) and AHPD (1) + PZ (2)

T	aqueous PZ (w_2)		AHPD (1) + PZ (2) + water: $100(w_1/w_2)$							
	6.88	13.76	1 / 6.88	1 /13.76	7 / 6.88	7 /13.76	13 / 6.88	13 / 13.76	19 / 6.88	19 / 13.76
298.15	1.000184	1.004535	1.002762	1.007333	1.018254	1.02308	1.034335	1.039527	1.051294	1.055913
303.15	0.998686	1.002826	1.001247	1.005596	1.016594	1.021184	1.032525	1.037474	1.049334	1.053702
308.15	0.996974	1.000928	0.999526	1.003676	1.014745	1.019123	1.030549	1.03527	1.047222	1.051354
313.15	0.995073	0.998855	0.997614	1.001582	1.012716	1.016903	1.028393	1.032921	1.044959	1.048867
318.15	0.99299	0.996614	0.995523	0.999322	1.010535	1.014536	1.026106	1.030436	1.042546	1.046239
323.15	0.990738	0.994214	0.993263	0.996908	1.008202	1.012023	1.02364	1.027827	1.04002	1.043525
328.15	0.988328	0.991664	0.99085	0.994342	1.005717	1.00937	1.021112	1.025088	1.037379	1.040693
333.15	0.98577	0.98897	0.988284	0.992918	1.003087	1.006588	1.018424	1.022229	1.034604	1.03778

Table 2. Fitting Parameters of Equation 1 for Density ρ (g.m-3) of Aqueous PZ (2) and AHPD (1) + PZ (2)

	aqueous PZ (w_2)		AHPD (1) + PZ (2) + water: $100(w_1/w_2)$							
	6.88	13.76	1 / 6.88	1 /13.76	7 / 6.88	7 /13.76	13 / 6.88	13 / 13.76	19 / 6.88	19 / 13.76
A_0	1.1240	1.1271	1.1380	1.1353	1.1483	1.1643	1.1708	1.1875	1.1942	1.2112
A_1	-0.0004	-0.0004	-0.0004	-0.0004	-0.0004	-0.0005	-0.0005	-0.0005	-0.0005	-0.0005
SD	0.004	0.004	0.016	0.009	0.011	0.009	0.014	0.002	0.007	0.006

Table 3. Viscosity η (mPa.S) of Aqueous PZ (2) and AHPD (1) + PZ (2)

T	aqueous PZ (w_2)		AHPD (1) + PZ (2) + water: $100(w_1/w_2)$							
K	6.88	13.76	1 / 6.88	1 /13.76	7 / 6.88	7 /13.76	13 / 6.88	13 / 13.76	19 / 6.88	19 / 13.76
298.15	1.08	1.39	1.11	1.33	1.6	1.69	1.85	2.1	2.61	3.26
303.15	0.96	1.27	0.99	1.21	1.42	1.51	1.68	1.88	2.33	2.8
308.15	0.86	1.16	0.87	1.08	1.26	1.35	1.48	1.68	2.06	2.45
313.15	0.78	1.01	0.8	0.94	1.12	1.19	1.32	1.51	1.83	2.12
318.15	0.71	0.90	0.71	0.85	0.99	1.06	1.19	1.37	1.57	1.84
323.15	0.65	0.79	0.64	0.74	0.89	0.97	1.08	1.22	1.41	1.58
333.15	0.54	0.65	0.52	0.61	0.74	0.8	0.91	1.04	1.16	1.24

Table 4. Fitting Parameters of Equation 4 for Viscosity η (mPa.S) of Aqueous PZ (2) and AHPD (1) + PZ (2)

	aqueous PZ (w_2)		AHPD (1) + PZ (2) + water: $100(w_1/w_2)$							
	6.88	13.76	1 / 6.88	1 /13.76	7 / 6.88	7 /13.76	13 / 6.88	13 / 13.76	19 / 6.88	19 / 13.76
A_0	-2.80	-3.08	-3.07	-3.17	-3.03	-2.90	-2.73	-2.62	-3.02	-3.51
A_1	843.76	965.45	929.61	985.91	964.10	932.34	892.37	877.66	1024.84	1199.22
SD	0.002	0.008	0.003	0.006	0.003	0.003	0.004	0.003	0.006	0.003

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

T	aqueous PZ (w_2)		AHPD (1) + PZ (2) + water: 100(w_1/w_2)							
K	6.88	13.76	1 / 6.88	1 /13.76	7 / 6.88	7 /13.76	13 / 6.88	13 / 13.76	19 / 6.88	19 / 13.76
303.15	69.71	65.16	60.91	59.42	57.52	54.45	53.21	51.8	49.21	47.11
308.15	68.99	64.19	60.08	58.49	56.61	53.48	52.11	50.69	48.42	46.15
313.15	68.39	63.14	59.17	57.52	55.75	52.63	51.19	49.99	47.41	45.29
318.15	67.68	62.2	58.5	56.52	54.98	51.55	50.29	49.02	46.39	44.5
323.15	67.06	60.87	57.68	55.61	54.19	50.58	49.04	48.25	45.51	43.47
333.15	65.88	58.98	56.11	53.55	52.65	48.67	47.35	46.41	43.67	41.71

Table 6. Fitting Parameters of Equation 2 for Surface tension σ(mN.m-1) of Aqueous PZ (2) and AHPD (1) + PZ (2)

	aqueous PZ (w_2)		AHPD (1) + PZ (2) + water: 100(w_1/w_2)							
	6.88	13.76	1 / 6.88	1 /13.76	7 / 6.88	7 /13.76	13 / 6.88	13 / 13.76	19 / 6.88	19 / 13.76
A_0	108.36	128.46	109.11	118.69	106.35	113.10	112.62	105.16	105.97	101.43
A_1	-0.1277	-0.2087	-0.1591	-0.1954	-0.1613	-0.1934	-0.1962	-0.1763	-0.1871	-0.1792
SD	0.046	0.089	0.050	0.036	0.057	0.042	0.097	0.077	0.054	0.048

Conclusion

Physical properties like density, viscosity and surface tension of aqueous solutions of PZ and (AHPD + PZ) were experimentally measured. The measurements were made over the temperature range of 298.15 K to 333.15 K. An overall decrease in all properties was observed with increasing temperature. Surface tension values also decreased with the increase of PZ and AHPD concentrations. The empirical correlations were used to correlate all the measured properties as a function of temperature

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