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Absorption of Green House Gas (CO₂) and Physical Properties of Aqueous Solutions of 2-Amino-2-Hydroxymethyl-1, 3-Propanediol and Di-Ethanolamine (AHPD+DEA) at Elevated Pressures

Ghulam Murshid, Azmi Mohd Shariff, Muhammad Azmi Bustam and Sami Ullah

Research Centre for Carbon Dioxide Capture (RCCO₂Cᵀᴹ), Universiti Teknologi PETRONAS, Tronoh, 31750, Perak, Malaysia

Abstract: Removal or capture of CO_2 from various industrial streams using amine based absorption process is the most widely used process in industry around the world. This is due to flexibility and applicability of the process for different applications. In chemical absorption, the absorbed substances undergo chemical reactions with the solvents which help to achieve high loadings but on the other hand leading to excessive energy consumption to recover solvents. Therefore, any alternative absorbent that could facilitate the separation of CO_2 from gas mixtures from various industrial streams, e.g., natural gas, flue gas from power plant, with high rate of reaction, high CO_2 absorption, cyclic capacity and negligible volatility, making them be highly desired. For this purpose, a new class of amines which is called Sterically Hindered Amines (SHA) is experimentally investigated in blend with DEA in order to combine the desired properties of two solvents in one hybrid mixture. Due to the cyclic structure of 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD), which is one of the sterically hindered amines, offers high rate of reaction and higher CO_2 absorption which makes this solvent a potential replacement of conventional amines. Therefore, the solubility of carbon dioxide (CO_2) in aqueous blends of 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD) and Di-ethanolamine (DEA), (DEA + AHPD) was measured at elevated pressure up to 1600 kPa for various hybrid mixtures concentrations. It was found that the addition of AHPD to the aqueous solutions of DEA gives significantly higher CO_2 loadings at higher pressures. The influence of pressure on solubility is found to be positive. However, solubility decreases with increase of temperature. Transport properties of aqueous blends of DEA+AHPD were also measured and correlated over the wide range of temperature. The total solvent concentration was kept at 30 wt% as per industrial interest. Density and viscosity values show the decreasing trend by increasing the temperature. However, viscosity of aqueous blends increase with the addition of AHPD concentration in the aqueous solutions.

Key words: CO_2, DEA, AHPD, elevated pressure

INTRODUCTION

Removal or capture of CO_2 from various industrial streams using amine based absorption process is the most widely used process in industry around the world (Paul and Mandal, 2006a; Sartori and Savage, 1983). This is due to flexibility and applicability of the process for different applications (Aroonwilas and Veawab, 2004). This process is mainly explained on the basis of two film theory that there is a mass transfer between gas and liquid phases. In other words, absorption is a process where molecules of one phase i.e., gas, are taken directly into the liquid phase (Aroonwilas and Tontiwachwuthikul, 1997; Aroonwilasa et al., 2003). In many technologically important processes, the chemical absorption is used instead of the physical process, e.g., absorption of carbon dioxide using alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA) and N-methyldiethanolamine (MDEA) (Xu et al., 1991; Paul and Mandal, 2006b). In chemical absorption, the absorbed substances undergo chemical reactions with the solvents which help to achieve high loadings but on the other hand leading to excessive energy consumption to recover solvents (Dragos et al., 1996). Therefore, any alternative absorbent that could facilitate the separation of CO_2 from gas mixtures from various industrial streams, e.g., natural gas, flue gas from power plant, with high rate of reaction, high CO_2 absorption cyclic capacity and negligible volatility, making them be highly desired. There is a new emerging class of amines to overcome the limitations of

Corresponding Author: Ghulam Murshid, Research Centre for Carbon Dioxide Capture (RCCO₂Cᵀᴹ), Universiti Teknologi PETRONAS, Tronoh, 31750, Perak, Malaysia

primary, secondary and tertiary amine is known as Sterically Hindered Amines (SHA). Sterically hindered amines such as 2-amino-2-methyl-1-propanol (AMP) and 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD) contains bulkier substituent are identified as most promising solvents due to lower stability of carbamate, higher CO_2 loading capacity and higher reactivity for CO_2 (Bougie and Iliuta, 2009, 2010; Teng and Mather, 1990).

Besides using the amines individually, the use of mixtures has also gained quite significant attraction. These blends combined the properties of higher absorption capacity of one amine (tertiary amines) with higher reaction rate of other amines (primary or secondary) and therefore high removal of acid gases can be achieved (Derks *et al.*, 2006; Li and Lie, 1994; Mandal *et al.*, 2003). There are different blends of primary, secondary and tertiary amines reported in literature. These blends are in various combinations of different amines such as MDEA+MEA, MDEA+DEA, DEA+MEA, MEA+AMP, DEA+AMP, DEA+PZ in order to reap the benefits offered by the significant characteristics of each amine in one solution (Bishnoi and Rochelle, 2000; Glasscock *et al.*, 1991; Jane and Li, 1997; Mondal, 2009). Unfortunately, the use of these blends has not attained great success due to the unavailability of insufficient findings thus needing more research to be conducted on its fundamentals. There is still need to explore more blends in order to find a suitable aqueous blend to minimize the CO_2 emissions from various industrial streams. However, no literature has been reported on the solubility and physical properties of aqueous blend of DEA with AHPD.

Therefore, in this study, the aqueous blends of DEA and AHPD are considered. DEA makes it suitable for the operation of lower to moderate range separation absorption process due to negligible vapor losses. The solvent AHPD is getting attention of researchers due to its cyclic structure which offers higher CO_2 loadings and fast rate of reaction and therefore can be a potential blend with DEA for effective removal of CO_2 emissions from various industries. In the study, solubility of CO_2 in aqueous blends of DEA+AHPD at pressure up to 1500 kPa is presented along with physical properties such as density and viscosity over the wide range of temperature. This equilibrium solubility data and physical properties such as density and viscosity are very important in designing of acid gas removal system (Paul and Mandal, 2006a; Sartori and Savage, 1983; Li and Lie, 1994).

METHODOLOGY

Materials: Carbon dioxide with a purity of 99.99% was purchased from Malaysian Oxygen Behrad (MOX Gases).

The solvents, AHPD and DEA of reagent grade (99.99%) were purchased from Merck, Malaysia. The bi-distilled water was used to prepare aqueous solutions. All the solutions were prepared gravimetrically using analytical balance (Mettler Toledo AS120S) within ±0.0001 g.

Solubility measurement: The solubility measurements were conducted in a high pressure solubility cell (SOLTEQ BP-22) shown in Fig. 1 as used by Harris *et al.* (2009). The set up consist of two vessels, pressurizing vessel with volume of 3 L and the equilibrium cell with the volume of 50 mL for CO_2 loading measurements.

Initially, both vessels were purged with nitrogen to remove any oxygen traces left in any of the cell. The pressure of CO_2 in the big cell was raised to 1600 kPa using air driven haskel pump. The pressure of the system was measured using digital pressure indicator (Druck DPI 150) with a precision of ±1.0 kPa for a range of 0-10,000 kPa. The temperature of the system was controlled by thermostat water bath Julabo by ±0.1°C and the inside temperature of mixing vessel and solubility cell was measured with YOKOGAVA (7653) digital thermometer with an accuracy of ±0.01°C. Vacuum was created in equilibrium cell and 5 mL of the aqueous solution was introduced using metering pump. The temperature of the cell was then adjusted to the desired value and pressure was noted. At this stage, solvent exists under its own vapor pressure P_v. The CO_2 was transferred from pressurized vessel to the equilibrium cell and the stirrer was turned on. The moles of CO_2 n_{CO_2} transferred were calculated using drop in pressure, volume of vessel and temperature by the following Eq. 1 (Jenab *et al.*, 2005):

$$n_{CO_2} = \frac{V_T}{RT_a}\left(\frac{P_1}{z_1} - \frac{P_2}{z_2}\right) \qquad (1)$$

where, V_T is the volume of the gas container (mixing vessel), z_1 and z_2 are the compressibility factors for each pressure (P_1 and P_2), R is the real gas constant and T_a is the ambient temperature. The compressibility factors were calculated using Peng Robinson equation of state (Jenab *et al.*, 2005). When there was no further drop in pressure inside equilibrium, cell indicating thermodynamic equilibrium is achieved, pressure value was recorded. The equilibrium pressure P_{CO_2} was calculated by the following Eq. 2:
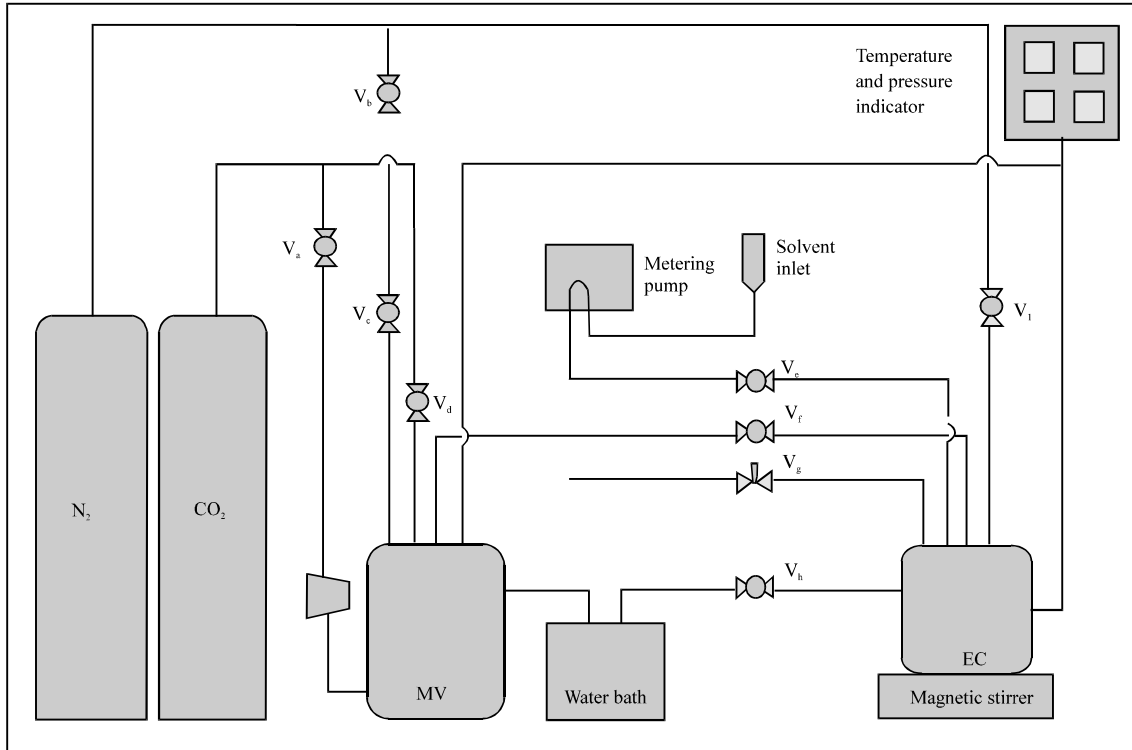
$$P_{CO_2} = P_T - P_V \qquad (2)$$

Fig. 1: High pressure solubility cell

where, PT is the total pressure and Pv is vapor pressure of solutions. The remaining moles of CO_2 in the gas phase ng were calculated by equilibrium pressure P_{CO_2}, temperature and overhead gas volume by using the following Eq. 3:

$$n_{CO_2}^g = \frac{V_g P_{CO_2}}{Z_{CO_2} RT} \qquad (3)$$

where, Vg is the gas volume in the equilibrium cell and T is the operating temperature. The moles of CO_2 in the liquid phase were then calculated from Eq. 4:

$$n_{CO_2}^l = n_{CO_2} - n_{CO_2}^g \qquad (4)$$

The solubility was then calculated as mol of CO_2 per mol of amine by using the following Eq. 5:

$$\alpha = \frac{n_{CO_2}^l}{n_{AM}} \qquad (5)$$

where, n_{AM} is the moles of AHPD in the liquid and calculated by the following Eq. 6:

$$n_{AM} = \frac{\rho V_l m_{AHPD}}{M_{AHPD}} \qquad (6)$$

where, ρ is the density of the aqueous solution of AHPD, V_l is the liquid volume in the cell, m_{AHPD} is the mass fraction of AHPD and M_{AHPD} is the molecular weight of AHPD.

Density measurement: Density of different aqueous blends of DEA+AHPD of various concentrations was measured using digital density meter (Anton Par, DMA-4500) with the measuring accuracy $\pm 5.0 \times 10^{-5}$ g cm^{-3}. The calibration of the apparatus was carried out each time before and after the measurement in order to get the accurate results. The water of Millipore quality was used in calibration process and the details can be found elsewhere (Murshid *et al.*, 2012). Data reported is the average of at least three measurements with temperature control accuracy of ± 0.01 K.

Viscosity measurement: Digital viscometer (Anton Par, model, Lovis- 2000M) was used to measure the viscosities of aqueous blends of DEA in AHPD (DEA+AHPD). Before and after each experiment, the viscometer was

carefully calibrated with Millipore quality water and the results were compared with the manufacturer value. For the measurement, the capillary was filled with the sample by the help of syringe, kept inside the viscometer until the set temperature was achieved and finally, the measurement was started. The reported viscosity data of aqueous blend of DEA+AHPD is the average of three measurements. The accuracy of the viscosity and temperature was estimated to be ±0.002 mPa.s and ±0.02 K, respectively.

RESULTS AND DISCUSSION

To validate the experimental method and solubility data, the solubility of 10% AHPD aqueous solutions at 323.15 K was measured and compared with the literature. These results along with the literature values are presented in Table 1. The measured data was in good agreement with the literature (Park *et al.*, 2003) with Average Absolute Deviation (AAD) of less than 3%. The AAD was calculated using the following Eq. 7:

$$AAD\,(\%) = \frac{1}{n}\sum \left|\frac{X_{exptl} - Y_{lit.}}{Y_{lit.}}\right| \times 100 \qquad (7)$$

where, n is the number of data points, X_{exptl} measured physical property and Y_{lit} physical property values from literature.

The solubility of CO_2 in aqueous solutions of DEA+AHPD was measured over the wide range of pressure up to 1600 kPa and at two industrially important temperatures i.e., 303.15 and 333.15 K. The total concentrations of aqueous blends were kept at 30% wt. The solubility results are presented in Table 2.

It can be observed from the reported solubility data that the addition of AHPD in to the aqueous solution of DEA facilitates the CO_2 solubility. The solubility of CO_2 tends to increase with increase in mass fractions of AHPD which could be due to the formation of bicarbonates formation which enhances the availability of free amines ion to capture more CO_2 as shown in Fig. 2 (Park *et al.*, 2003).

On the other hand, Fig. 3 shows that the pressure has a positive impact on CO_2 loadings in all studied solutions as the solubility tends to increase by increasing the pressure. However, it is observed that solubility decrease at higher temperature which could be due to the evaporation of solvent at higher temperatures as shown in Fig. 4.

The density and viscosity of aqueous blends of DEA+AHPD were measured over the wide range of temperature and correlated as a function of temperature.
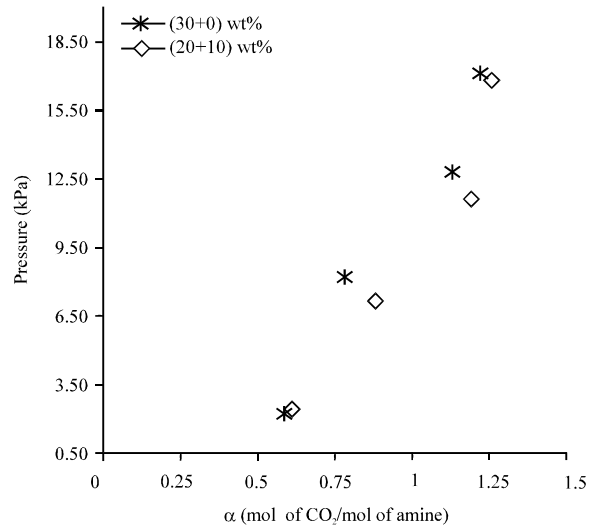

Fig. 2: Effect of AHPD on solubility of CO_2 in aqueous solution of DEA at 303.15 K; DEA+AHPD

Table 1: Solubility of CO_2 in 10% mass AHPD and comparison with literature

Park *et al.* (2003)		Present study	
P/kPa	α	P/kPa	α
127.3	0.749	151.5	0.896
167.6	0.918	345.6	0.974
342.8	0.992	610.3	1.101
602	1.12	1045	1.113
1506.6	1.286	1985	1.385

Table 2: Solubility of CO_2 in aqueous blends of (DEA+AHPD)

DEA+AHPD Wt (%)	T = 303.15 K		T = 333.15 K	
	P_{co_2} / kP a	α	P_{co_2} / kP a	α
30+0	245	0.5897	241	0.5741
	824	0.7834	736	0.6963
	1265	1.1151	1197	0.9858
	1678	1.2069	1714	1.1767
20+10	265	0.6154	318	0.5442
	723	0.8794	855	0.746
	1158	1.1748	1167	1.0909
	1658	1.2387	1736	1.2008
10+20	287	0.6529	330	0.5904
	638	1.0268	733	0.8614
	1126	1.2038	1143	1.1196
	1680	1.2814	1635	1.2508

Table 3: Density ρ (g cm^{-3}) of Aqueous solutions of (DEA+AHPD)

	(DEA+AHPD) wt (%)		
T (K)	(30+0)	(20+10)	(10+20)
303.15	1.07445	1.05883	1.0446
308.15	1.07227	1.05666	1.04229
313.15	1.06993	1.05436	1.03998
318.15	1.0674	1.05192	1.03754
323.15	1.06482	1.04932	1.03498
328.15	1.06204	1.04653	1.0323
333.15	1.05924	1.04347	1.02949

The results are presented in Table 3 and 4, respectively. The density values decrease by increasing both the
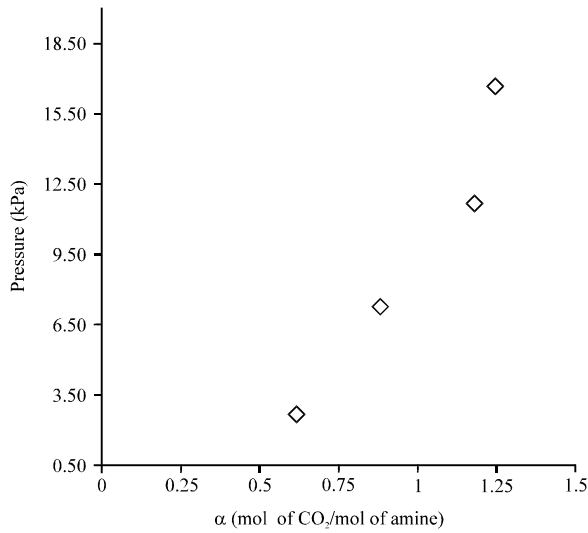
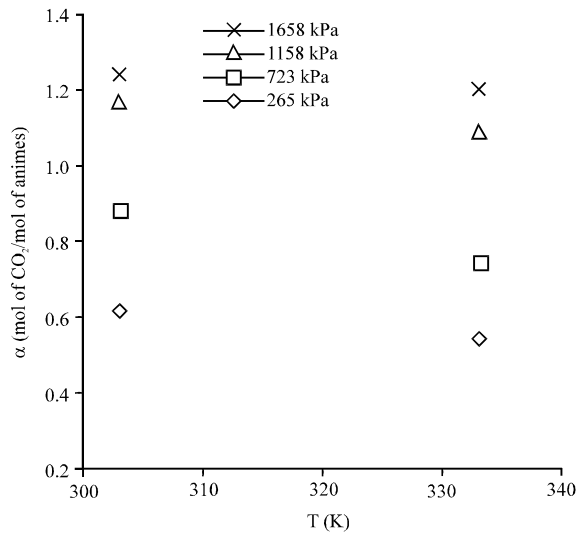Fig. 3: Effect of pressure on solubility of CO_2 in aqueous blend of DEA with AHPD (20+10) at 303.15 K

Fig. 5: Density of aqueous blends of (DEA+AHPD) at various temperatures and concentrations

Table 4: Viscosity η (mPas) of aqueous solutions of (DEA+AHPD)

	(DEA+AHPD) wt (%)		
T (K)	(30+0)	(20+10)	(10+20)
303.15	2.692	2.315	2.439
308.15	2.329	2.013	2.144
313.15	2.037	1.765	1.877
318.15	1.772	1.563	1.655
323.15	1.575	1.406	1.487
328.15	1.41	1.264	1.33
333.15	1.257	1.141	1.21

Table 5: Fitting parameters of equation 1 for density ρ (g m^{-3}) and viscosity of aqueous blends of (DEA+AHPD)

Parameters	wt (%)	DEA+APHD				
		A_1	A_2	$10^6. A_3$	R^2	S.D
ρ (g m^{-3})	0+30	0.96911	0.00126	-2.6	0.99997	0.002884
	10+20	0.86638	0.00167	-3.4	0.99996	0.003873
	20+0	0.9762	0.00088	-2.2	0.99998	0.001449
η (mPa.S)	wt (%)	A_1	A_2	$10^4. A_3$	R^2	S.D
	0+30	104.47245	-0.59868	8.671	0.99958	0.010613
	10+20	86.73775	-0.49725	7.214	0.99929	0.01073
	20+10	88.44059	-0.50503	7.3	0.99979	0.00588

Fig. 4: Effect of temperature on solubility of CO_2 in aqueous blends of DEA+AHPD

concentration of AHPD and temperature as shown in Fig. 5. This could be due to the wider spaces between the blend molecules at high temperature.

The experimentally measured viscosity data for aqueous blends of DEA+AHPD at wide range of temperature are reported in Table 4. The reported results show that the viscosity decreases with increasing temperature as shown in the Fig. 6. This can be due to decrease in internal resistance of molecules at higher 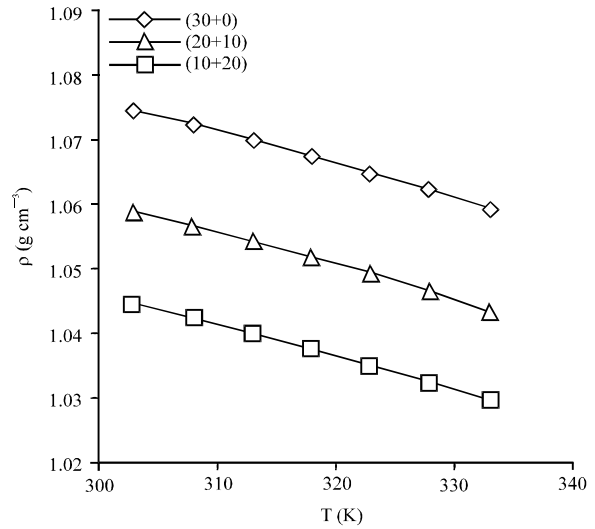temperatures which allows the molecules to flow relatively easy which reduces the viscosity of solutions. However, the viscosity of the aqueous blends increase with increasing concentration of AHPD in aqueous DEA solutions.

The higher concentrated solutions have high viscosity which could be due to the more molecular resistance in higher concentration solutions. Both physical properties were correlated using the following empirical correlation (Eq. 8):

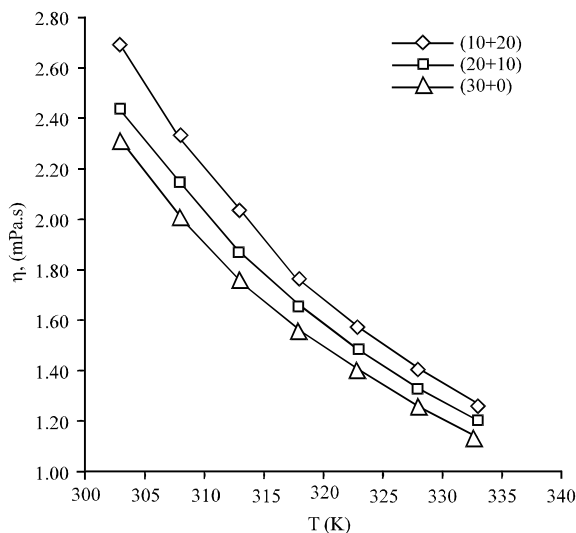$$X = A_1 + A_2 \left(\frac{T}{K}\right) + A_3 \left(\frac{T}{K}\right)^2 \tag{8}$$

Fig. 6: Viscosity of aqueous blends of (DEA+AHPD) at various temperatures

where, X is the density or viscosity, A_1, A_2 and A_3 are the fitting parameters. The Standard Deviation (SD) between experimental and calculated physical properties values were computed by the following Eq. 9 and presented in Table 5.

$$SD = \left[\frac{\sum_{i}^{n} (Z_{exptl} - Z_{calcd})^2}{n} \right]^{1/2} \qquad (9)$$

There is a good agreement found between calculated and experimental values as indicated by the SD values.

CONCLUSION

Solubility of CO_2 in aqueous blends of DEA+AHPD was experimentally measured from lower to higher range of pressure at various temperatures and concentrations. It has been found that the solubility of CO_2 is influenced by the addition of AHPD in to the aqueous solutions of DEA. However, relatively lower CO_2 loading were measured at higher temperature. Density and viscosity of aqueous blends were also measured for wide range of temperature and correlated as a function of temperature. The density and viscosity values decrease by increasing temperature irrespective of any concentration of aqueous blend. However, viscosity of aqueous solutions of DEA increases by the addition of AHPD. The density values

decrease with the addition AHPD. There was a good agreement between experimental and calculated physical properties.

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