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Thermo Physical Analysis of 2-Amino-2-methyl-1-propanol Solvent for Carbon Dioxide Removal

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Removal of acid gases such as carbon dioxide (CO_2) is normally carried out by aqueous solutions of alkanolamines. The traditional amines used for acid gas removal include; mono-ethanolamine (MEA), di-ethanolamine (DEA) and N-methyldiethanolamine (MDEA). There is a need to investigate new solvents to minimize the carbon emissions since the traditional amines have low CO_2 loading capacity and require high energy for regeneration. Recently, a new class of amines, sterically hindered amines is identified as one of the potential solvent for acid gas removal due to their relatively higher CO_2 absorption capacity, low heat of regeneration and higher values of rate constant. One of the identified solvent that has potential for commercialization is sterically hindered amine known as 2-amino-2-methyl-1-propoanol (AMP). The investigation of thermo-physical properties of this solvent is essential in the design and optimization for smooth operation of acid gas removal process. The density, viscosity, surface tension and refractive index are the most important physical properties for this purpose which is presented in this paper. These properties of aqueous solutions of 2-amino-2-methyl-1-propanol (AMP) are investigated over the industrially important temperature range of 298.15 K to 333.15 K. The thermal analysis of aqueous solutions was also carried out using TGA (Thermal gravity analyzer) with the heating rate of 10 $°C \cdot min^{-1}$ under nitrogen (N_2) environment in order to investigate the thermal stability of the solvent. All the investigated properties are correlated as a function of temperature for ease of usage in the design of acid gas removal system. The correlated and measured data are in good agreement.

1. Introduction

In the awake of global response for the protection of environment and sustainable development, the removal, disposal and useful utilization of CO_2 evolved from different sources is becoming a challenge with time. The major sources of CO_2 emission include the burning of fossil fuels, coal fired power plants, oil refining, hydrogen production, several industrial processes and sweetening of natural gas (Purba and Taharuddin, 2010). CO_2 is one of the green house gases that contribute to the global warming (Gomez-Castro et al. 2010). Removal of acid gases such as CO_2 from the industrial streams is commonly carried out by aqueous solutions of alkanolamines. The traditional amines used for acid gas removal include; mono-ethanolamine (MEA), di-ethanolamine (DEA) and N-methyldiethanolamine (MDEA) (Collodi and Wheeler, 2010). These amines have their operational and absorption limitations (high heat of regeneration, low absorption capacity, corrosion and foaming). Recently a new class of amines, sterically

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hindered amines is suggested as one of the attractive amine for acid gas removal due to their relatively higher CO_2 absorption capacity and higher values of rate constant (Bougie et al. 2010). One of the sterically hindered amine, 2-amino-2-methyl-1-propoanol (AMP) (Xu et al. 1991) is the potential absorbent for CO_2 removal with relatively high CO_2 loading, selectivity and efficient regeneration due to the advantage of producing unstable carbamate. The thermophysical properties of such solvents are important in designing and smooth operation of the process. The density and viscosity are important in the design of acid gas contactor, rate modeling and reaction rate calculations. Surface tension can affect the hydrodynamics and the rate of mass transfer between liquid and gaseous streams in the column. Thermal stability helps to set the feasible operating temperature range of process in order to avoid thermal loses of the solvent. Refractive index can be used to identify the solvent and solute concentrations (Braun et al. 2001; Park et al. 2003; Paul et al. 2006). Therefore in this paper the physical properties such as density, viscosity, surface tension, refractive index and thermal decomposition were experimentally measured. All the properties were measured for AMP concentrations (8.91, 17.82, and 26.73) wt % over the wide range of temperature from 298.15 K to 333.15 K that has potential for practical application. All the measured properties were correlated as a function of temperature for ease of usage in the design of acid gas removal system.

2. Experimental Section

2.1 Materials and Methods

AMP 95% was purchased from Merck, Malaysia. It was used without further purification. The bi-distilled water was used to prepare solutions. All the solutions were prepared gravimetrically using an analytical balance (Mettler Toledo AS120S) with a measuring accuracy of ±0.0001g. 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 %.

2.2 Density and Viscosity

A digital vibrating glass U-tube densitometer (DMA 5000, Anton Paar) with the measuring accuracy of ± 5.0 x 10^{-6} g.cm^{-3} was used to measure the density of binary solutions of AMP. 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 experimental uncertainty of measured density at corresponding temperature was estimated to be as ± 4.0 x 10^{-6} g·cm^{-3} and ± 0.02 K. Kinematic viscosities were measured using calibrated Ubbelohde viscometers of appropriate sizes. The viscometers were immersed in a thermostatic bath (Tamson, TVB445) with temperature controlled accuracy of ± 0.02 K. The efflux time was 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.

2.3 Refractive Index and Surface Tension

The refractive index was measured using a digital refractometer (Atago, RX-5000 alpha) with a measuring accuracy of ± 4.0 x 10^{-5}. The measured values of refractive index cover the temperature range from (298.15 to 333.15) K with 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 measured experimental uncertainty at a given temperature was found ± 4.0 x 10^{-5} and ± 0.05 K.

Surface tension was measured using IFT 700 (VINCI Technologies) with a precision of ± 0.03 mN.m^{-1}. The pendent drop method was used to measure the surface tension. All the values were measured between the temperature ranges of 298.15 K to 333.15 K with temperature controlled accuracy of ± 0.2 K. The reported data is the average of 5 data points. The measured experimental uncertainties at a corresponding temperature were found ± 0.04 mN.m^{-1} and ± 0.2 K

2.4 Thermal Decomposition

Thermal stability of binary solutions of AMP was investigated using a thermo gravimetric analyzer (TGA, Perkin-Elmer) at temperatures (303.15 to 773.15) K. The effect of decomposition on samples were studied at a heating rate of 10°C ·min^{-1} with the temperature accuracy of ± 3 °C The nitrogen was supplied at the rate of 20 mL.min^{-1}

3. Results and Discussion

The experimentally measured physical property (density, viscosity, refractive index and surface tension) values are presented in Table 1. The density and surface tension values decreased with the increase of both temperature and AMP concentrations. Whereby, an increase in viscosity and refractive index values were observed with the addition of AMP to the aqueous solutions. The density, refractive index and surface tension were correlated as function of temperature as per following Eq. 1 whereas the viscosity data was correlated using Eq. 2.

$$Z = A_o + A_1 / T \quad (1)$$

$$\log(\eta) = A_o + A_1 / T \quad (2)$$

Table 1. Physical properties of Binary solutions of AMP

T	AMP *wt* %					
K	8.91%	17.82%	26.73%	8.91%	17.82%	26.73%
	Density g/cm^{-3}			Viscosity (mPa.S)		
298.15	0.99700	0.99617	0.99581	1.16	1.73	2.70
303.15	0.99437	0.99415	0.99347	1.03	1.51	2.26
308.15	0.99256	0.99195	0.99130	0.91	1.37	1.94
313.15	0.99055	0.98958	0.98843	0.82	1.19	1.64
318.15	0.98836	0.98705	0.98541	0.72	1.02	1.46
323.15	0.98600	0.98437	0.98259	0.65	0.91	1.28
328.15	0.98348	0.98155	0.97938	0.59	0.79	1.14
333.15	0.98080	0.97859	0.97643	0.56	0.69	1.00
	Refractive index(nD)			Surface tension (mN.m^{-1})		
298.15	1.34713	1.35961	1.37238	63.10	56.03	43.01
303.15	1.34659	1.35901	1.37170	62.18	55.21	41.89
308.15	1.34612	1.35819	1.37099	60.99	54.12	40.70
313.15	1.34531	1.35773	1.37012	59.77	53.09	39.64
323.15	1.34399	1.35669	1.36878	58.87	52.18	38.65
333.15	1.34268	1.35571	1.36754	57.08	50.85	36.89

Where Z is density, refractive index and surface tension, η is the viscosity, A_o, A_1 are the 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 standard deviations .The following Eq. 3 was used to calculate standard deviations

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

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

Table 2. Fitting Parameters of Eq. 1&2 to Correlate Physical Properties of AMP

Physical Property	*wt* 8.93%			*wt* 17.82%			*wt* 26.74%		
	A_0	A_0	SD	A_0	A_1	SD	A_0	A_0	SD
ρ/g.m^{-3}	1.1317	-0.0005	0.0003	1.1468	-0.0005	0.0004	1.1634	-0.0006	0.0004
η/mPa.s	2.8349	-0.0093	0.01	3.6339	-0.0114	0.2	2.8349	-0.0093	0.43
nD	1.3858	-0.0001	0.0001	1.3925	-0.0001	0.0001	1.4141	-0.0001	0.0001
σ/mN.m-1	112.996	-0.1682	0.35	99.392	-0.1463	0.32	92.905	-0.1685	0.35

Thermal stability of binary solutions of AMP was investigated using TGA. The results of thermal decomposition of all samples are presented in Table 3. The values are presented in terms of T_{start} (start temperature for decomposition), T_{onset} (intersection of baseline weight and the tangent of weight vs temperature curve) and T_f (final decomposition temperature).The thermo plots of all systems studied here are presented in Figure 1, 2, 3 and 4.

Table 3. Thermal decomposition of Pure and Binary solutions of AMP

T	AMP *wt* %			
°C	Pure	8.91 %	17.82 %	26.73 %
Tstart	33.55	30.97	29.45	28.22
Tonset/°C	95.74	64.89	64.89, 115.11	68.28, 102.19
Tf/°C	250.93	376.28	366.28	367.95

The binary mixtures of AMP have shown lower onset values as compared to pure AMP. In Figure 2, lower onset temperature (64.89°C) shows that initially water molecules were decomposed. The onset temperature and two step decomposition in Figure 3 and 4 also shows that initially water molecules were decomposed followed by AMP molecules in second step. The final decomposition temperature of binary solutions of

AMP is relatively higher than the pure AMP which shows that strong bonding between AMP and water molecules.

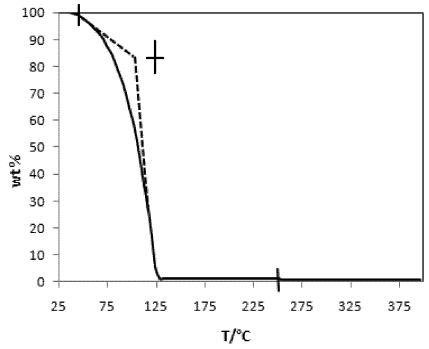

Figure 1: Thermo plot of pure AMP
T_{start} = 33.55 °C, wt %= 99.92, T_{onset} = 95.74 °C , wt % = 87.31
T_{final} = 250.93 °C, wt % = 0.567

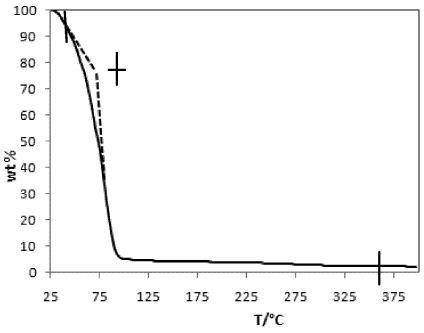

Figure 2: Thermo plot of binary solution of AMP (8.91) wt %, T_{start} = 30.97 °C, wt = 99.56 %, wt %, T_{onset} = 64.89 °C, wt = 85.55 %, T_{final} = 368.28 °C, wt = 0.886 %

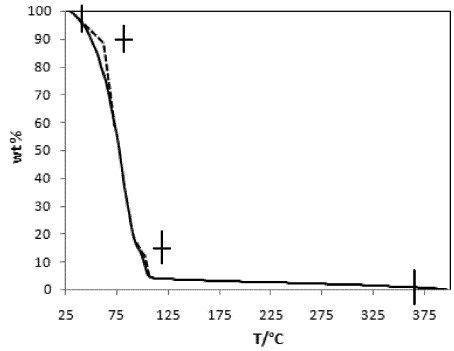

Figure 3: Thermo plot of binary solution of AMP (17.82) wt %, T_{start} = 29.45 °C, wt = 99.56 %, wt %, T_{onset} = 64.89 °C, wt = 85.55 %, 115.11 °C, wt = 19.86 %, T_{final} = 366.28 °C, wt = 0.586 %

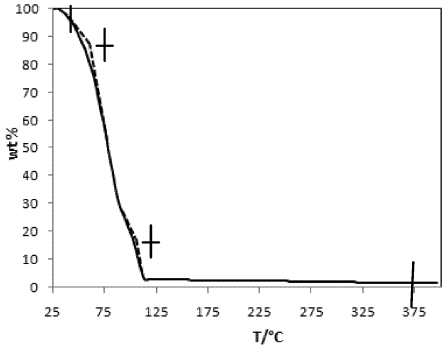

Figure 4: plot of binary solution of AMP (26.73) wt %, T_{start} = 28.22 °C, wt = 99.60 %, T_{onset} = 68.28 °C, wt = 82.96 % & 102.19 °C, wt = 12.67 %, T_{final} = 367.95 °C, wt = 0.55 %

4. Conclusions

Physical properties including density, viscosity, surface tension and refractive index of binary solutions of AMP were experimentally measured. The measurements were made over the wide range of temperature from 298.15 K to 333.15 K and AMP binary solutions concentrations of (8.91 to 26.73) wt %. The decrease in all properties of binary solutions was observed with increase of temperature. All the measured properties were correlated as a function temperature and good agreement was found with the measured and correlated values. The thermal stability of binary solutions of AMP was also investigated over the temperature range of 303.15 K to 673.15 K with a heating rate of 10 °C·min^{-1} and the N_2 flow rate of 10 mL·min^{-1}. The thermal stability increases by increasing the AMP concentration in the solution. The correlated properties can be used in the design of acid gas removal system within the investigated range of conditions.

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