

Thermophysical Analysis of Aqueous Solutions of 2-Amino-2-hydroxymethyl-1, 3-propanediol (Potential CO₂ Removal Solvent from Gaseous Streams)

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Abstract

In the wake of global response for the protection of environment and sustainable development, the removal, disposal and useful utilization of carbon dioxide (CO₂) evolved from different sources is becoming a challenge with time. CO₂ is one of the major green house gas and responsible for the climate changes on earth. The major sources of CO₂ emission include the burning of fossil fuel, coal fired power plants, oil refining, hydrogen production, several industrial processes and sweetening of natural gas. Removal of acid gases from gaseous streams (sweetening of natural gas) such as CO₂ is 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). These amines have their operational and absorption limitations (high heat of regeneration, low absorption, corrosion and foaming). Therefore, there is need of developing new technologies, new solvents and their blends and optimization of existing processes to minimize the carbon emissions. Recently, a new class of amines (2-Amino-2-hydroxymethyl-1,3-propanediol), sterically hindered amines is suggested as one of the attractive amine for acid gas removal due to their relatively higher CO₂ absorption capacity and higher values of rate constant. The thermophysical analysis of such solvents is important in designing and smooth operation of the process. Thermophysical properties such as density, viscosity and thermal stability of 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD) were experimentally measured. All the experimental measurements were made over the wide range of temperatures from (298.15 to 333.15) K and mass fractions of AHPD (13, 19 and 25) %. The measured physical properties were correlated as a function of temperature. Thermal decomposition of pure and aqueous solutions of AHPD was investigated using a thermo gravimetric analyzer (TGA) at a heating rate of 10 K·min⁻¹.

Introduction

Alkanolamines are used for the removal of acid gases such as carbon dioxide (CO₂) and hydrogen sulphide

(H₂S) in the process of different industrial gaseous streams through absorption process. The most industrially used alkanolamines include; mono-ethanolamine (MEA), di-ethanolamine (DEA), N-methyldiethanolamine (MDEA)¹. Recently, sterically hindered amines are proposed as potential solvents for acid gas removal due to their unique cyclic structure and high CO₂ loading²⁻⁶. The investigated solvent in this paper, 2-Amino-2-hydroxymethyl-1,3-propanediol (AHPD) is also a sterically hindered amine^{6,7}. The solubility data and kinetic studies show that AHPD is a good potential solvent for acid gas removal from industrial streams of our interest⁸⁻¹¹. The knowledge of physical properties of solvents is essential for design, hydrodynamics and transfer rate calculations of absorption process¹²⁻¹⁵. A literature review^{7,8,12} on physical properties of AHPD shows that the available open literature is scarce and limited in temperatures and compositions. In the present work, density, viscosity and thermal stability of aqueous solutions of AHPD are reported. The physical properties were investigated over the mass fraction range of (13, 19 and 25) % and temperature ranging from (298.15 to 333.15) K. All the experimentally measured physical properties were correlated as a function of temperature. Thermal stability of aqueous solutions was also investigated using TGA at heating rate of 10 K·min⁻¹ under N₂ flow rate of 20 mL·min⁻¹.

Table. 1
Density (g/cm³) of AHPD + H₂O

T/K	AHPD (wt) %			Ref. 8
	13%	19%	25%	
298.15	1.0305	1.0471	1.0628	
303.15	1.0288	1.0453	1.0609	1.0613
308.15	1.0270	1.0434	1.0588	
313.15	1.0249	1.0412	1.0566	1.0571
318.15	1.0228	1.0389	1.0542	
323.15	1.0204	1.0365	1.0517	1.0525
328.15	1.0179	1.0340	1.0491	
333.15	1.0153	1.0313	1.0464	

Experimental Section

Materials and Methods

AHPD of reagent grade (99.99 %) was purchased from Merck, Malaysia and was used without further purification. The bi-distilled water was used to prepare aqueous solutions of AHPD. All the solutions were

prepared gravimetrically using an analytical balance (Mettler Toledo AS120S) within ± 0.0001 g.

Table. 2
Viscosity (mPa.s) of AHPD + H₂O

AHPD (wt) %				
T/K	13%	19%	25%	Ref. 8
298.15	1.18	1.46	1.97	
303.15	1.05	1.28	1.77	1.79
308.15	0.94	1.14	1.54	
313.15	0.85	1.03	1.37	1.40
318.15	0.77	0.93	1.22	
323.15	0.71	0.84	1.11	1.13
328.15	0.64	0.77	1.02	
333.15	0.59	0.70	0.90	0.92

Table. 3
Thermal Decomposition of AHPD + H₂O

AHPD (wt) %			
T/K	13	19	25
T _{start} /K	306.15	306.15	306.15
T _{onset} /K	345.15 & 479	342.6 & 477.15	335.29 & 489
T _f /K	665.15	666.15	665.15

Table 4
Fitting Parameters of Eq. 2 & 3

Physical Property	A ₀	A ₁	SD
wt 13 %			
$\rho/g.m^{-3}$	1.1609	-0.0004	0.0112
$\eta/mPa.s$	-2.7633	843.9904	0.001
wt 19%			
$\rho/g.m^{-3}$	1.1827	-0.0005	0.0148
$\eta/mPa.s$	-2.849	896.7343	0.003
wt 25%			
$\rho/g.m^{-3}$	1.2037	-0.0005	0.0092
$\eta/mPa.s$	-2.9309	961.7999	0.004

Density: The density of aqueous solutions of AHPD was measured using a digital vibrating glass U-tube densitometer (DMA 5000, Anton Paar) within $\pm 5.0 \times 10^{-5}$ g.cm⁻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 K to 333.15 K. 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 measurements. The experimental

uncertainty of measured density was estimated to be as $\pm 4.0 \times 10^{-5}$ g.cm⁻³

Viscosity: The kinematic viscosities of aqueous solutions of AHPD were measured using a calibrated Ubbelohde viscometer of appropriate size. The viscometer containing AHPD solutions was immersed in thermostatic bath (Tamson, TVB445). The bath temperature was controlled within ± 0.01 K. The sample was immersed for at least 15 minutes to get equilibrate with the set point before any measurement. The efflux time was then measured using a manual stop watch capable of measuring time within ± 0.01 s. The kinematic viscosities were calculated by multiplying the efflux time with the viscometer constant as per following eq 1.

$$v = Ct \quad (1)$$

where v 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 viscosity was calculated by multiplying the corresponding measured density with kinematic viscosity. The uncertainty of experimental results was found to be ± 0.03 mPa. S.

Thermal Decomposition: Thermal stability of aqueous AHPD solutions was investigated using a thermo gravimetric analyzer (Perkin-Elmer) at temperatures 303.15 K to 773.15 K. The effect of decomposition on samples were studied at a heating rate of 10 K .min⁻¹. The nitrogen was supplied at the rate of 20 ml .min⁻¹

Results and Discussion

The measured densities and viscosities of solutions of (AHPD + H₂O) are presented in Table 1 and Table 2 respectively as a function of temperature and AHPD mass fractions. All the physical properties were investigated for the temperature ranging from 298.15 K to 333.15 K. The experimental densities and viscosities of present work are in good agreement with the literature were compared with the work of Park et al.⁸ The average relative deviations of density and viscosity for aqueous solutions of mass fraction of 25 % have been found to be 0.05 % and 1.5 % respectively from the work of Park et al.⁸ as shown in Figures 1 and 2. The measured densities and viscosities values increased with increase in AHPD mass fractions in the solutions. The density and viscosity results were correlated as a function of temperature using eq 2 and eq 3 respectively:

$$Z = A_0 + A_1(T/K) \quad (2)$$

$$\log(\eta) = A_0 + A_1/(T/K) \quad (3)$$

Where Z is density and η is viscosity, A_0 , A_1 are the fitting parameters and T is the temperature. The fitting parameters were calculated using the method of least square and presented in Table 4 along with standard deviations. The eq 4 was used to calculated standard deviations of all the measured physical properties

$$SD = \left[\sum_i^n (Z - Z_{calc})^2 / n \right]^{1/2} \quad (4)$$

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

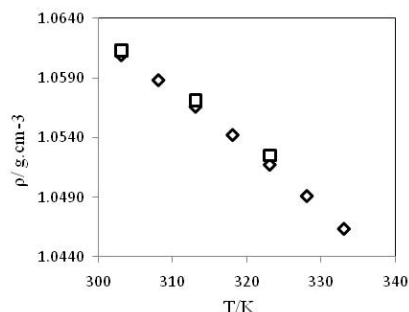


Figure 1. Densities of 2-Amino-2-methyl-1,3-propanediol (1) + Water (2) at (25) mass % from 298.15 K to 333.15 K: \blacklozenge this work; \square Park et al.⁸

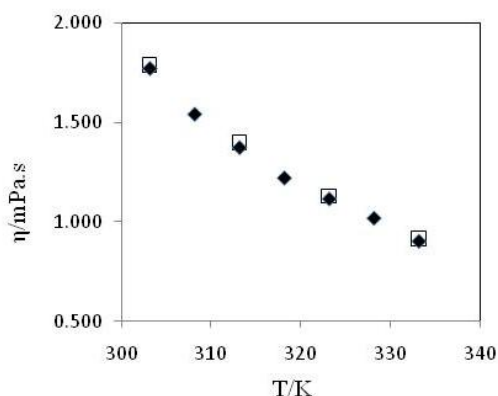


Figure 2. Viscosities of 2-Amino-2-methyl-1,3-propanediol (1) + Water (2) at (25 mass %) from 298.15 K to 333.15 K: \blacklozenge this work; \square Park et al.⁸

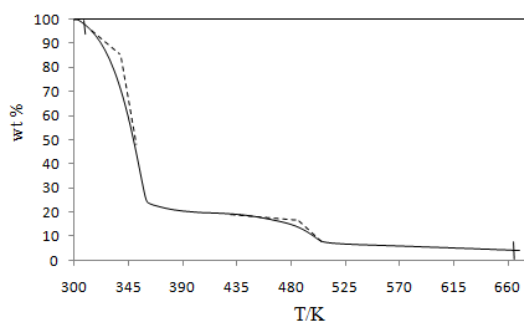


Figure 3(a): Plot for thermal decomposition of aqueous solution of AHPD (13 mass %) as weight percent loss (wt %) vs temperature (T/K); T_{start} =306.15 at 99.65 wt %, T_{onset} =345.15, 479 at (83.5, 20.10) wt %, T_f =665.14 at 2.65 wt %

Thermal stability of aqueous solutions of AHPD was evaluated using a thermo-gravimetric analyzer (TGA). The results of thermal decomposition of all the samples are presented in Table 3 in terms of T_{start} (start temperature for decomposition), $T_{(onset)}$ (intersection of baseline mass fraction and the tangent of mass fraction vs temperature curve) and T_f (final decomposition temperature). Figure 3 (a, b, c) shows the decomposition of pure AHPD and aqueous solutions of AHPD (13, 19 and 25) mass % respectively. The aqueous solutions of AHPD show lower T_{start} values as compared to pure AHPD. The onset temperature and two step degradation of aqueous solution show that initially water molecules were evaporated followed by the degradation of AHPD molecules. The addition of AHPD to the aqueous solutions did not show any significant effect on the final decomposition temperature.

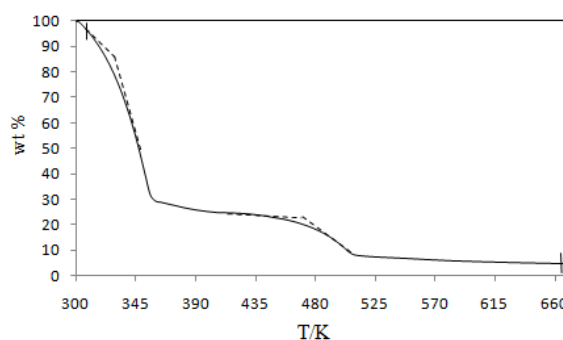


Figure 3(b): Plot for thermal decomposition of aqueous solution of AHPD (19 mass %) as weight percent loss (wt %) vs temperature (T/K); T_{start} =306.15 at 98.10 wt %, T_{onset} =342.60, 477.15 at (78.33, 25.65) wt % , T_f =666.15 at 1.01 wt %

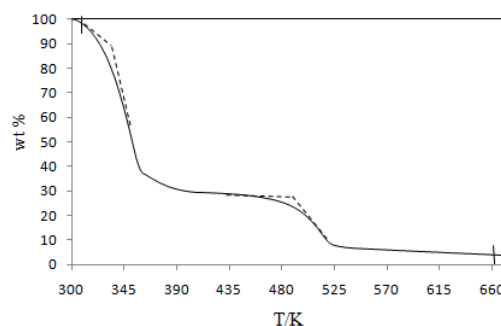


Figure 3 (c): Plot for thermal decomposition of aqueous solution of AHPD (25 mass %) as weight percent loss (wt %) vs temperature (T/K); T_{start} =306.15 °C at 99.18 wt %, T_{onset} =335.29 , 489 at (85.65, 29.88) wt % , T_f =665.15 at 1.21 wt %

Conclusion

Physical properties like density and viscosity aqueous solutions of AHPD were studied over the wide

range of temperature ranging from (298.15 to 333.15) K. An overall decrease in all the measured physical properties was observed with increasing the temperature. The physical properties measured, were also correlated as a function of temperature. Thermal decomposition of pure AHPD and aqueous solutions were also investigated using a thermogravimetric analyzer.

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