CHEMICAL ENGINEERING TRANSACTIONS
VOL. 106, 2023
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Jeng Shiun Lim, Nor Alafiza Yunus, Peck Loo Kiew, Hon Huin Chin

ISBN 979-12-81206-05-2; **ISSN** 2283-9216
DOI: 10.3303/CET23106217

Synthesis and Characterization of β-Alanine Based Aqueous Solutions for CO_2 Capture

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In this work, Aminoethylpiperazine (APZ) activated aqueous solutions of potassium β-alaninate (K-βala) were synthesized. There were three different APZ activated solutions (3 wt %, 6 wt %, and 9 wt%) were synthesized for a fixed 10 wt% concentration of potassium β-alaninate (K-βala). The physical properties such as density and viscosity were experimentally measured for the above different concentrations in the temperatures range of 298.15 to 333.15 K. All measured physical properties were observed to increase when increasing the mass concentration of APZ and decreasing by increasing the temperature. The experimental results were regressed as a function of temperature and the solution mass concentration using suitable correlations. The correlations showed good agreement with the experimentally measured physical properties, therefore the correlations can predict the properties at the given temperature and concentration with excellent accuracy.

1. Introduction

Greenhouse gases emission is considered as the main cause of global warming and the disturbance of the temperature stability of the earth (Herrmann, 2014). In fact, the elevation of global warming to 2 °C or above pre-industrial temperature will place the earth in the threat of irreversible environmental changes, including the nonstop melting of polar land ice (Singh, 2011).

Referring to a statistical study reported in 2016, about 84 % of the total man-made greenhouse gases emission resulted from CO_2 contribution (Ring, 2019). The contribution of the industrial revolution is approximately 30% of the total CO_2 emission, which resulted mainly from burning of fossil fuels (Mazria, 2019). Hence, CO_2 capture from effluent industrial gas streams is one of the important requirements for the reduction of CO_2 emissions.

Several competing technologies are being used by industry to separate CO_2 from the effluent gas streams. Presently, there are three primary pathways used in capturing CO_2 which include; post-combustion, oxy-fuel, and pre-combustion(Singh, 2011). Post-combustion carbon capture is considered as the most studied capture process among the three technologies since there is a good experience of this process in industrial applications. Post-combustion capture can be performed using four different CO_2 capture technologies including adsorption, membranes, cryogenics, and absorption (Singh, 2011). Chemical absorption using chemical solvents (absorbents) is a mature technology to recover CO_2 from the flue gas because it can be added to any existing power plant as a tail-end process (Dugas, 2009). In the process of chemical absorption, the gas is absorbed using a selected solvent by a chemical reaction and then the solvent can be regenerated in a stripping column at elevated temperature to be used again in the capture process (Chakravarti et al., 2001).

One of the common types of CO_2 capture solvents are alkanolamines, which include monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA), N-methyldiethanolamine (MDEA), diglycolamine (DGA) and their mixtures (Majchrowicz, 2014). Furthermore, many mixtures of amines were introduced and used with different additives to promote absorption rate or prevent corrosion (Singh, 2011).

In recent times, amino acid salt solutions attracted the interest of researchers as a new carbon dioxide solvent which could overcome the drawbacks of alkanolamines. Amino acids are characterized as a non-toxic and environmentally friendly solvent because they present in nature and exist in the human body (Rao and Rubin, 2002).

Paper Received: 19 April 2023; Revised: 25 August 2023; Accepted: 12 October 2023
Please cite this article as: Balushi S.M.A., Nasser J.T., Ghulam M., Ma'Awali S.S.A., Mjalli F.S., 2023, Synthesis and Characterization of -Alanine Based Aqueous Solutions for CO2 Capture, Chemical Engineering Transactions, 106, 1297-1302 DOI:10.3303/CET23106217

Despite the fact that the amino acid solutions are more expensive than alkanolamines, their advantages over the conventional absorbents make them attractive and prevail over this obstacle (Lerche, 2012). These advantages could include their low volatility, high stability toward thermal and oxidative degradation, low viscosities, and high reactivity toward CO_2 (Kumar et al., 2001). Furthermore, amino acid solutions have suitable binding energy with CO_2 and high biodegradability (Mazinani et al., 2015). Besides, the solution possesses an ionic structure having lower volatility than alkanolamines when hydroxides such as potassium, sodium, and lithium are added to amino acids.

Lately, interest to improve the CO_2 capture process is raised by mixing amino acid-based solvents with some activated additives called, promoters (Syalsabila et al., 2018). Several chemicals have been proposed as promoters for CO_2 capture process. Piperazine is one of the chemicals used as a promoter since it significantly improves the CO_2 absorption rate and enhances the mass transfer in the scrubbing process (Privalova et al., 2013). Hamzehie and Najibi (2016) investigated the CO_2 absorption in blends of potassium glycinate and piperazine. The obtained data showed that the CO_2 absorption experienced a significant increase after the addition of the piperazine as a promoter.

β-alanine is one example of an amino acid. This solvent is a linear, primary amino acid. The performance of these amino acid solutions in capturing CO_2 was examined by many previous studies. Furthermore, Murshid (2015) examined the performance of the addition of piperazine as a promoter to the solution of β-alanine to provide extra advantages to the β-alanine based solutions. The piperazine activated aqueous solutions helps to enhance the CO_2 solubility by inducing higher formation of bicarbamates in the solution. Further, the addition of piperazine not only would enhance CO_2 absorption capacity of the solution but also reduce the regeneration energy (Lu et al., 2011). To the best of our knowledge, no data on the CO_2 loading is presented in the literature for the system of Potassium βalaninate (K-βala) blended with Aminoethylpiperazine (APZ). Therefore, this study focuses on this blended system of amino acids to further explore its application to minimize CO_2 emissions.

To fully utilize the solvent properties in designing the absorption process, it is important to measure such properties. Since no such data is found in the open literature for this particular amino acid aqueous system, Therefore, this study aims to measure the physical properties of the selected solvent, at different temperatures and mass concentrations. Density and viscosity of the selected blend were studied at temperatures ranging from 298.15 to 333.15 K. This range of temperature is important since the absorber operating temperature lies within this range. Therefore, it is essential to measure and evaluate the properties within this range which are consequently required in designing of any absorption column. Therefore, the properties such as density and viscosity were measured and correlations were developed as a function of temperature and solution concentration.

2. Experimental section

2.1. Materials

β- Alanine (βala) ($C_3H_7NO_2$) and Aminoethylpiperazine (APZ) ($C_6H_{15}N_3$) used in this work were purchased from Sigma-Aldrich, both with purity of ≥99 %. Potassium Hydroxide (KOH) (purity ≥85%) was purchased from Merck. Bi-distilled water with purity of >99 % was used in the solvent preparation. All the chemicals were used without further purification.

2.2 Solvent preparation

The aqueous solution of Potassium β-alaninate (K-βala) was prepared by neutralizing βala with an equimolar amount of KOH which were then dissolved in deionized water in a volumetric flask. In the selected system of (Potassium β-alaninate (K-βala) blended with Aminoethylpiperazine APZ), the concentration of K-βala was kept constant at 10 wt % and APZ was varied at (3, 6 and 9 wt %). All solvents were prepared gravimetrically using an electronic analytical balance (Uni Bloc, model AUW220D) with a measuring accuracy of ±0.001g. A similar procedure of preparation was reported in the literature (Aftab et al., 2017).

2.3 Physical properties measurements

The density of the solvents used in this research was measured using a density meter (a digital U-tube DMA 4500, Anton Paar). Density was measured in the range of temperature 298.15 to 333.15 K. The uncertainty of temperature is ± 0.01 K. About 1 mL of sample was slowly injected into the U-tube measuring cell using a syringe. Then, the density meter was activated to record the data in the device memory. The uncertainties of density and temperature were ±9 $x10^{-5}$ g cm^{-3} and ±0.01 K.

Viscosity measurements of all studied solvents were done using a rotation viscometer (Rheolab QC, Anton Paar). It provides flexible utilization by its simple arrangement with an accuracy of ± 0.3%. The ranges of viscosity, speed, and shear rate are, 1 to 10^9 mPas, 0.01 to 1,200 min^{-1}, and 10^{-2} to 4,000 s^{-1}. The temperature is regulated using an external water bath (Techne-Tempette TE-8A), which provides a temperature range

between -20 and +180 °C. The cup is cleaned before and after each experiment with a volatile solvent. Calibration of the device using distilled water is important to ensure the precision of the results. The device collects data and stores it using a software program.

3. Results and discussion

Before performing the required density or viscosity measurements for the selected solvent, both equipment was tested using distilled water and the results were compared with the literature as shown in Table 1. For ease of comparison, the Average Absolute Deviation (% AAD) was calculated using Eq(1) and used to examine the accuracy of the device. According to the calculated % AAD (0.00560 shows good agreement between measured and literature data as shown in Table 1.

$$\%AAD = \frac{1}{n}\sum\left|\frac{x_{exp}-x_{lit}}{x_{lit}}\right| \times 100 \quad (1)$$

Where x_{exp} is the experimental result, x_{lit} is the literature data and n is the number of data points. The viscometer (Rheolab QC, Anton Paar) is calibrated using distilled water to ensure the accuracy of the viscosity measurements. The results were then compared with the literature. Table 1 shows the experimental and literature data at three different temperatures (303.15, 313.15, and 333.15 K). The % AAD of 1.0280 was reported, which is an indication of the good accuracy of the experimental measurements. The small deviation obtained may be due to the variation in purity and measuring apparatus.

Table 1: Calibration of density and viscosity equipment using pure water

Density (ρ) g·cm^{-3}				Viscosity (μ) mPa.s			
T/K	This Work	Literature*	% AAD	T/K	This Work	Literature**	% AAD
303.15	0.99566	0.99565		303.15	0.803	0.7975	
313.15	0.99220	0.99222	0.00560	313.15	0.651	0.6532	1.0280
333.15	0.98334	0.98320		333.15	0.457	0.4666	

*(Wagner & Kretzschmar, 2008), **(Garg et al., 2017)

3.1 Density

The density of Potassium β-Alaninate (K-βala) promoted with APZ aqueous solution was measured at APZ mass concentrations of 3, 6, and 9 wt %, and at five different temperatures, 298.15, 303.15, 308.15, 313.15, 323.15, and 333.15 K. The mass concentration of K-βala was fixed at 10 wt% in all experiments. The density data were used then to find the best fit correlation for density at a given temperature and mass concentration by using MATLAB Software. The obtained correlation is shown in Eq(2), where ρ represents the density, x is the mass concentration, T is the temperature and a(i) are the fitting parameters for this specific solvent as tabulated in Table 2.

$$\rho\,(x\,,T)\; = (a_1 + a_2 x)\,(a_3 + a_4 T) \quad (2)$$

Table 2: Fitting parameters for the empirical correlations of density and viscosity

Density		Viscosity	
a1	-6.37	a1	10.19
a2	0.00079	a2	0.32
a3	680.64	a3	0.04
a4	-0.26	a4	-106.23
% AAD	3.04x10^{-4}	a5	0.38
R^2	0.9980	% AAD	5.45x10^{-2}
		R^2	0.9829

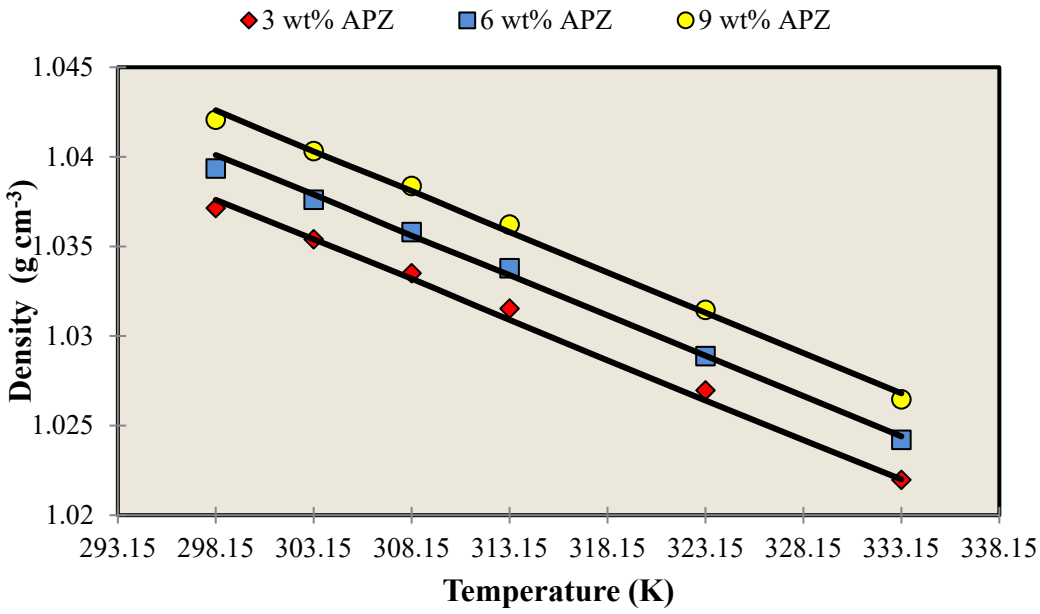

Figure 1: Experimental and the correlated density data of K-βala+APZ

Thus, the empirical correlation has an excellent agreement with the results obtained from the density measurements with %AAD and coefficient of determination (R^2) of 3.04×10^{-4} and 0.9980. Furthermore, the figure clearly illustrated the relation of density with the temperature and the mass concentration. The density decreases linearly by increasing the temperature from 298.15 to 333.15 K at fixed mass concentration. This behavior can be justified by the formation of wider spaces between the molecules as a result of increasing the temperature, which as a consequence increases the overall volume of the solution and hence reduces the density of the solvent. In fact, this behavior is expected, since the system subjected to liquid thermal expansion observed for other liquid systems. In contrast, the density of the solvent is directly proportional to increasing the mass concentration. This could be due to interaction between the solute and water by increasing the concentration. From the obtained data, the minimum density (1.02197 g/cm^3) was obtained at the highest temperature (333.15 K) and the lowest mass concentration (3 wt % APZ). At fixed temperature (303.15 K) the density was observed to increase from 1.0354 to 1.04032 g/cm^3 as increasing the mass concentration of APZ. Similar observations on the density behavior were reported in the literature (Murshid, 2015).

3.2 Viscosity

The viscosity of K-βala+APZ was measured at five different temperatures, 298.15, 303.15, 308.15, 313.15, 323.15 and 333.15 K. The mass concentration of K-βala was fixed at 10 wt% and APZ was added at three different concentrations (3, 6, 9 wt %).

These viscosity results were then correlated using MATLAB Software to find the best equation that represented the viscosity at any given temperature and mass concentration in the studied ranges. The obtained correlation is illustrated in Eq(3).

$$\mu\,(x.T) = \frac{a_1 + a_2 x + a_3 x^2}{a_4 + a_5 T} \qquad (3)$$

Where μ is the predicted viscosity of the solvent, x is the mass concentration of K-βala, T is the temperature and a(i) are the fitting parameters of this correlation. The parameters which are accurately fitted to the data are tabulated in Table 2.

Figure 2 shows the plot of the experimental and the correlated viscosity data at different temperatures for each mass concentration. The data were in good agreement with each other, indicating the validation of the obtained correlation for the viscosity calculation of this system at the specified temperatures and mass concentrations. The reported %AAD and R^2 are 5.45×10^{-2} and 0.9829.

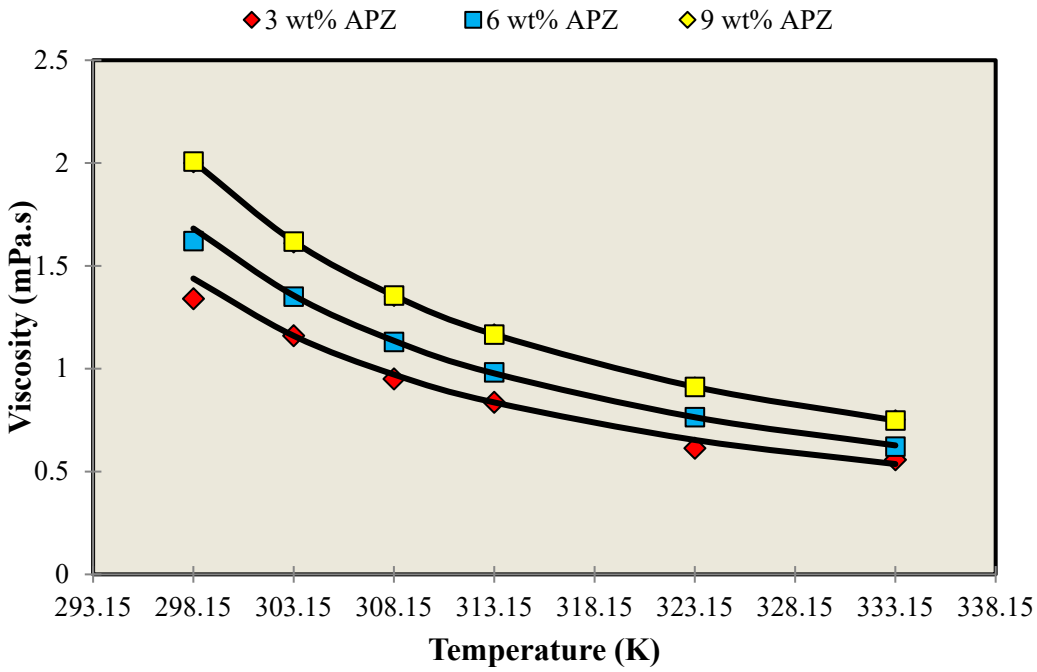

Figure 2: Experimental and the correlated viscosity data of K-βala +APZ

The effects of temperature and mass concentration on the viscosity were illustrated in Figure 2. The viscosity decreased exponentially by elevating the temperature from (298.15 to 333.15 K) at constant mass concentration. This effect can be explained by the reduction of the intermolecular forces at higher temperatures, which as a result increases the fluidity of the solvent and decreases its viscosity by reducing its resistance to flow. On the other hand, increasing the mass concentration of APZ from 3 to 9 wt% increases the molecular resistance and consequently increases the viscosity of the solvent. By increasing the temperature from 298.15 to 333.15, the viscosity experienced a gradual reduction in its values from 2 to 0.752 mPa.s, at 9 wt% APZ. Conversely, at a fixed temperature (exp. 313.15 K), the viscosity increased from 0.836 to 1.17 mPa.s by changing the mass concentration of APZ from 3 to 9 wt %. Furthermore, it is obvious that the differences of the viscosity get smaller and smaller with increasing the temperature. The same trends have been reported in previous literature (Murshid et al., 2017).

4. Conclusions

The physical properties of APZ activated aqueous solutions of potassium β-Alanine (K-βala) were measured in the temperature range of 298.15 to 333.15 K. The effect of temperature and mass concentration for all properties was investigated. The density and viscosity values tend to decrease by increasing temperature for any fixed concentration. However, the values aforementioned properties tend to increase by increasing the salt concentration in the aqueous solution. The availability of this data for the particular solvent system studied in this work is of immense importance which can be useful in designing CO_2 capture processes and other related engineering processes.

Acknowledgement

We would like to express our thanks to Sultan Qaboos University for providing us both the technical and funding resources to complete this work.

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