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Thermo-Physical Properties and Solubility of CO_2 in Piperazine Activated Aqueous Solutions of β-Alanine

Ghulam Murshid

***Abstract*—**Carbon dioxide is one of the major greenhouse gas (GHG) contributors. It is an obligation of the industry to reduce the amount of carbon dioxide emission to the acceptable limits. Tremendous research and studies are reported in the past and still the quest to find the suitable and economical solution of this problem needed to be explored in order to develop the most plausible absorber for carbon dioxide removal. Amino acids can be potential alternate solvents for carbon dioxide capture from gaseous streams. This is due to its ability to resist oxidative degradation, low volatility and its ionic structure. In addition, the introduction of promoter-like piperazine to amino acid helps to further enhance the solubility. In this work, the effect of piperazine on thermo physical properties and solubility of β-Alanine aqueous solutions were studied for various concentrations. The measured physicochemical properties data was correlated as a function of temperature using least-squares method and the correlation parameters are reported together with it respective standard deviations. The effect of activator piperazine on the CO_2 loading performance of selected amino acid under high-pressure conditions (1bar to 10bar) at temperature range of (30 to 60)^oC was also studied. Solubility of CO_2 decreases with increasing temperature and increases with increasing pressure. Quadratic representation of solubility using Response Surface Methodology (RSM) shows that the most important parameter to optimize solubility is system pressure. The addition of promoter increases the solubility effect of the solvent.

***Keywords*—**Amino acids, CO_2, Global warming, Solubility.

I. Introduction

GLOBAL warming and climate change are resulted from greenhouse gases that are emitted to the atmosphere from various sources such as power plants and sweetening of natural gas processes [1]. The energy demand is expected to rise by 50%, which will contribute the CO_2 emissions by 52% in 2030 [1], [2]. Carbon dioxide is believed to be the major contributor for this problem. Most carbon dioxide comes from energy generation from the combustion of fossil fuels. If combined with water, it has the ability to corrode and destroy pipelines. Absorption, adsorption, membrane, and cryogenic process are the technologies, which are used by the industry [2], [3]. Optimizations of absorption by various type chemical solvents are continuously being improved and developed by researchers to get high reactivity, low solvent cost, low absorption of hydrocarbon, and low oxidative degradation. Previously, alkanolamines like monoethanolamine (MEA) and diethanolamine (DEA) are used as CO_2 absorber due to fast reaction kinetics and low solvent cost. However, MEA induced to more oxygen degradation, metal corrosion, and high regeneration energy [4], [5]. Amino acids are identical to alkanolamines because of the presence of similar functional group in the molecule but equipped with unique characteristics. Amino acids are considered to be the alternative of alkanolamines because of its ability to resist oxidative degradation, low volatility due to its ionic structure and higher surface tension compared to alkanolamines [4], [6]. Modification of amino acid based solvents to enhance the characteristic towards CO_2 absorption by blending promoters and other compounds is one of the research interest in CO_2 capture technology [6], [7]. In this work, non-sterically hindered linear amino acid β-alanine (BA) is blended with promoter piperazine to measure the physiochemical and thermodynamic solubility of these mixtures. BA forms more (bi) carbonate compared to MEA which can directly enhance the CO_2 absorption [8]. However, the blends of alkanolamines with piperazine are getting good attention by the researchers around the world [10]. Meanwhile, piperazine (PZ) is a proven activator for alkanolamines due to the rapid formation of carbamate with CO_2. Piperazine activated MDEA technology was patterned by BASF [9]. The aqueous solution of BA and PZ will induce high formation of bicarbamate which is expected to enhance the CO_2 solubility in the aqueous mixture. Thermodynamic properties and the thermodynamic equilibrium solubility of CO_2 are essential parameters to design the absorber and to understand the intermolecular interactions of gas and solvent molecules [4], [6]. Therefore, in this research work, the physicochemical properties and solubility of CO_2 in PZ activated β-Alanine aqueous solutions (BA+PZ) were measured over a wide range of temperature, pressure, and aqueous solution concentrations.

Murshid, G. is with the Department of Petroleum and Chemical Engineering of Sultan Qaboos University, Muscat. Oman (phone: +968-2414-2546; fax: +968-2414-1354; e-mail: g.murshid@squ.edu.om).

II. Materials and Methods

A. Materials

The main reagent for this project is linear amino acid, β-Alanine (≥ 99% pure) and promoter piperazine (≥ 99% pure) were obtained from Merck Sdn. Bhd, Malaysia. Different blends of (BA + PZ) were prepared using double-distilled water. The blending ratio of aqueous solutions were kept maximum to 30 wt % which were prepared using gravimetrically with analytical balance (Mettler Toledo AS120S) with the accuracy of ± 0.0001 g. Carbon dioxide with 99.99% purity was obtained from Malaysia Oxygen Berhad (MOX Gasses).

B. Methodology

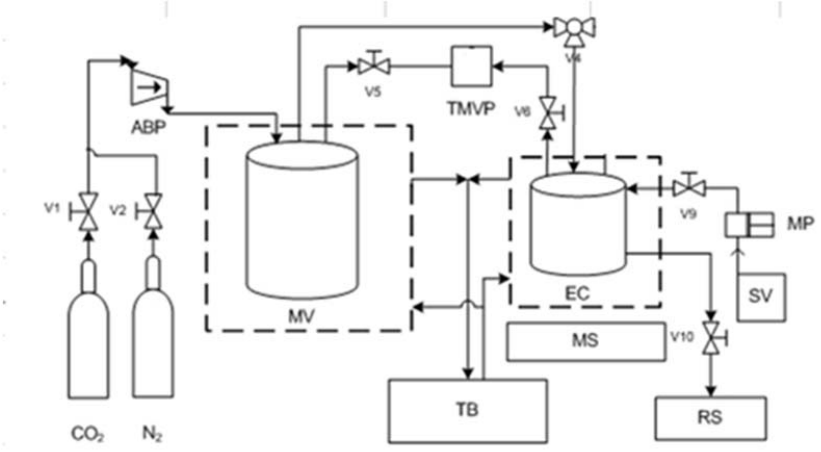
Density of different blends of (BA + PZ) are measured

using digital Anton Par density meter (DMA-4500M). The density and temperature accuracy of the equipment is ± 0.00003g.cm^{-3} and ±0.01K respectively. The equipment was calibrated by using standard water Millipore quality repeatedly after completing each measurement to minimize the error. Data averages of three measurements were reported. Viscosities of piperazine activated aqueous solution of B-alanine are measured using digital rolling ball Anton Par micro viscometer (Lovis-2000M). The equipment accuracy is up to 0.5%. The estimated viscosity and temperature uncertainties were ±7.10-3mPa.s and ± 0.02K respectively. The equipment was calibrated repeatedly by using standard water Millipore quality after completing each measurement. Samples were kept inside viscometer until the set temperature reach equilibrium conditions before measurement are taken. Triplicate readings were taken and reported as average in the data [7]

High-pressure solubility cell as shows in Fig. 1 was used to measure the solubility of CO_2 in PZ activated aqueous solutions of BA. It mainly consist of two vessels named, mixing vessel and solubility cell. 5mL of solvent was introduced to the equilibrium cell using metering pump. Pressure of the system was adjusted to the desired pressure. CO_2 was transferred from mixing vessel to equilibrium cell. The pressure of the cell was noticed to drop with time and it gets stabilized in 6 to 8 hours in every run. Details of the method and calculation were essentially the same as reported in literature and it can also be found in previous works [11]-[13]. The solubility of CO_2 in terms of moles of solvent mixture was calculated from (1);

$$\alpha = \frac{n^{l}CO_2}{n_{solution}} \quad (1)$$

where α is solubility, $n^{l}_{CO_2}$ is moles of CO_2 in liquid phase and $n_{solution}$ are the moles of aqueous solution.



ABP: Air driven gas booster pump, MV: Mixing Vessel, EC: Equilibrium Cell, TMVP: Turbo molecular vaccum pump, TB: Thermostat waterbath, MS: Magnetic stirrer, MP: Metering pump

Fig. 1 High-pressure gas solubility setup

The solubility data was further used for optimization using the Response Surface Methodology (RSM) in order to investigate the influence of operating parameters on the CO_2 solubility [14]. The formulation of a second order equation that describes the process is as follows;

$$B=b_o+b_1X_1+b_2X_2+b_3X_3+b_{11}X_{12}+b_{22}X_{22}+b_{33}X_{32}+b_{12}X_1X_2+b_{13}X_1X_3+b_{23}X_2X_3 \quad (2)$$

B is the solubility, b_o is the intercept term, b_1, b_2 and b_3 are the linear coefficients, b_{11}, b_{22}, b_{33}, are quadratic equations, b_{12}, b_{13}, b_{23}, b_{24} are interactive coefficients and X_1, X_2, X_3 are the independent variables.

III. Results and Discussion

Physicochemical properties such as density and viscosity, of piperazine activated aqueous solution of β-Alanine (BA + PZ) were measured experimentally for three various concentrations of BA and PZ over a wide range of temperature. The plot of density versus temperature is shown in Fig. 2. From the plot, it can be seen that, as the concentration of β-Alanine increases, the density is increased. However, with increasing temperature, the density of piperazine activated aqueous solution decreases. This is because, at higher temperature range, the spacing between molecules is wider. The density trend of piperazine activated aqueous solution of B-alanine is similar to previous reported work that uses piperazine as promoter.

The plot of viscosity versus temperature is shown in Fig. 3. Analysis of the result shows that the viscosity decreases as the temperature increase. This could be due to the internal resistance of molecules decreases with the increasing temperature and directly allow the solution molecules to flow easily, thus reducing its viscosity. Besides that, the increase in mass percentage of B-alanine will increase the viscosity of the solutions. High piperazine mass percentage may lead to a rise in viscosity due to higher molecular resistance.

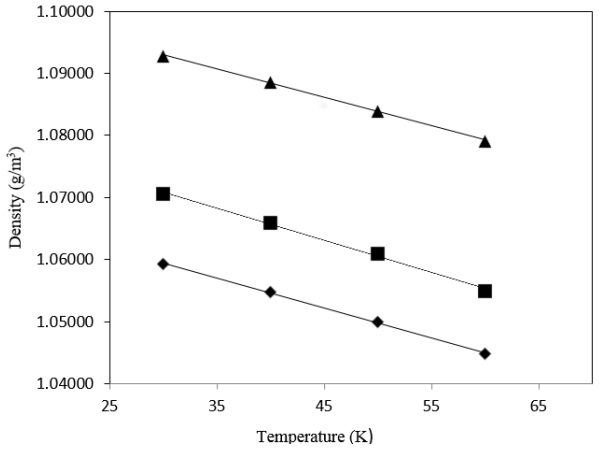


Fig. 2 Density of aqueous solution of (BALA + PZ) at various temperatures: ◆ (16 + 14) wt%, ■ (22 + 8) wt %, ▲ (28 + 2) wt %

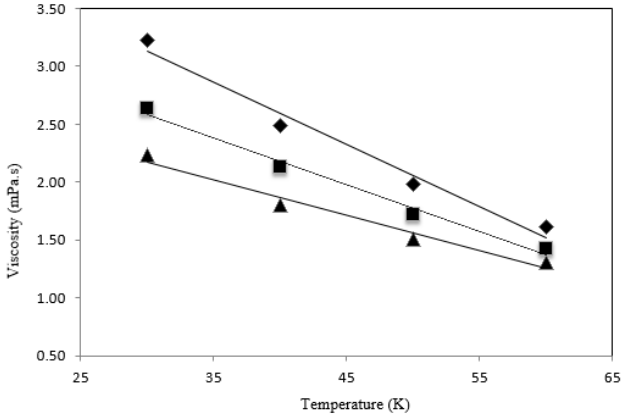


Fig. 3 Viscosity of aqueous solution of (BALA + PZ) at various temperatures: ◆ (16 + 14) wt%, ■ (22 + 8) wt %, ▲ (28 + 2) wt %

TABLE I
FITTING PARAMETERS A_o, A_1 AND SD

Parameter (BA + PZ)	A_o	A_1	SD
(16 + 14) wt %			
Density (ρ/ g.cm-3)	1.0738	-0.0005	0.0000949
Viscosity (η /mPa.s)	4.7402	-0.0536	0.0944902
(22 + 8) wt %			
Density (ρ/ g.cm-3)	1.0864	-0.0005	0.0008851
Viscosity (η /mPa.s)	3.8022	-0.0405	0.0530354
(28 + 2) wt %			
Density (ρ/ g.cm-3)	1.1069	-0.0005	0.0018222
Viscosity (η /mPa.s)	3.0971	-0.0307	0.0584206

The measured data of density and viscosity was correlated as a function of temperature using linear regression.

$$Y = A_o + A_1(T/^oC) \quad (3)$$

where Y are density or viscosity, A_o and A_1 are fitting parameters and T is temperature. The method of least square was used to calculate the fitting parameters as shown in Table I along with the standard deviations (SD)

$$SD = \sqrt{\frac{\sum_i^n (X_{\exp} - X_{cal})^2}{n}} \quad (4)$$

where SD is standard deviations, n is number of experimental data points, X_{exp} ,X_{calc} are experimental and calculated data respectively.

TABLE II
ANOVA ANALYSIS COEFFICIENTS OF SOLUBILITY DATA

Sources	Sum of square	DF	Mean Square	F Value	Prob > F
Model	8.64	9	0.96	24.29	<0.0001 significant
A	0.33	1	0.33	8.29	0.0164
B	6.74	1	6.74	170.58	< 0.0001
C	0.48	1	0.48	12.03	0.0060
A2	0.093	1	0.093	2.36	0.1556
B2	0.065	1	0.065	1.65	0.2276
C2	0.039	1	0.039	0.99	0.3439
AB	0.13	1	0.13	3.23	0.1027
AC	0.060	1	0.060	1.51	0.2478
BC	0.14	1	0.14	3.49	0.0914
Residual	0.4	10	0.0040		
Lack of Fit	0.4	5	0.079		
Pure Error	0.000	5	0.000		

The solubility of CO_2 in aqueous solutions of B-alanine and Piperazine (BALA + PZ) was also measured for the various concentrations of (BA + PZ) mixture at industrially important temperatures of 30, 40 and 50°C. The effect of pressure on CO_2 solubility was also studied as pressure was varied from 1 bar to 10 bar in order to cover the wide range of application of CO_2 absorption process. The results obtained from the solubility experiment showed that the solubility ranged from 0.20 to 2.29 depending on the process parameters.

The solubility results and the effect of various variable such as Temperature, Pressure and Concentrations on it are summarized in Figs. 4-6. It can be observed from Fig. 4 that pressure has positive impact on solubility since the solubility increases by increasing pressure from 1 bar to 10 bar. However, high temperatures are not suitable for effective CO_2 absorption due to high vapor pressure of solvents. The effect of concentration on solubility is represented in Fig. 5 and it is evident that the addition of PZ to the BA aqueous solution influence the CO_2 solubility in the mixture. The similar trends are shows in Fig. 6 that at any concentration of aqueous mixture, solubility decreases by increasing temperature. Therefore, for effective absorption in the absorber, high pressure and low temperature are recommended which is the usual practice for absorber. ANOVA (analysis of variance) was used to further study the effect of process parameters such as centration, temperature, and pressure to develop a correlation. The result of the analysis is the quadratic model as shown below:

Solubility (α) = 3.37077-0.17195*A+0.31828*B-0.0069406*C+5.111364E-003*A^2+7.60943E-003*B^2+1.19091E-003*C^2 -4.67593E-003*AB- 1.43750E-003*AC-2.91667E-003*BC

The quadratic model represents solubility as a response, A as the coded value for B-alanine and piperazine concentration, B as the coded value for pressure, C as the coded value for temperature. The value of mean square (R^2) from the analysis of variance (ANOVA) describes if the model fits best to the experimental data. The closer the value of R^2 to unity, better the the model fit to the experimental data. The R^2 value for this particular model was 0.956, which is close to unity as also shown in Fig. 7 that observed and model predicted results are in well match. The given equation is reliable and applicable in representing the solubility in piperazine activated aqueous solutions and can also be used to simulate the reaction. The statistical ANOVA analysis for the quadratic model shows that the parameter B (pressure) has the highest F-value of 170.59 as shown in Table II, which indicates that the most influencing parameter for the solubility as compared to the other three parameters. The similar effect was observed during the experiments. Generally, the expected trend is solubility increases with decreasing temperature and increasing pressure.

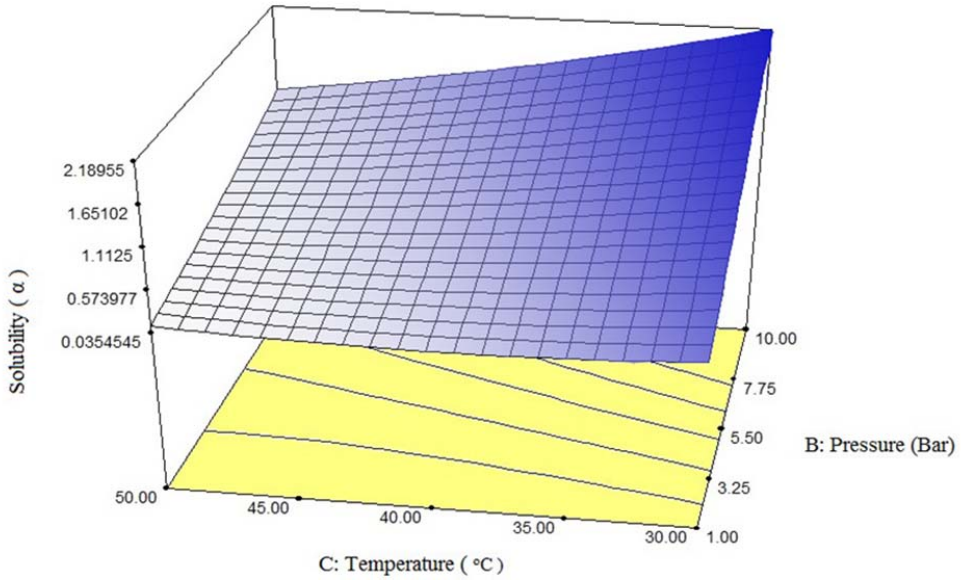


Fig. 4 Effect of temperature and pressure on solubility of CO_2 in aqueous solutions of (BA + PZ)

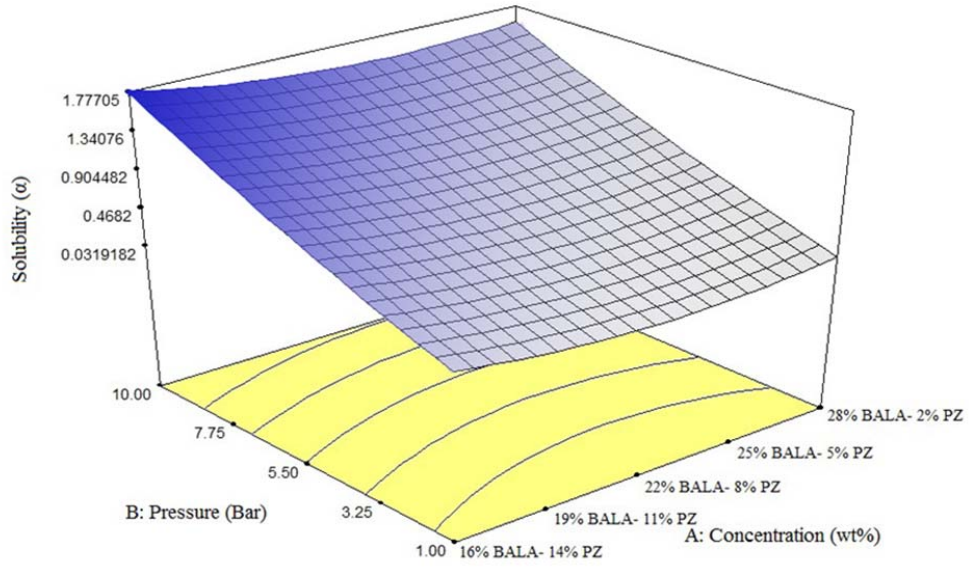


Fig. 5 Effect of concentration on solubility of CO_2 in aqueous solutions of (BA + PZ)

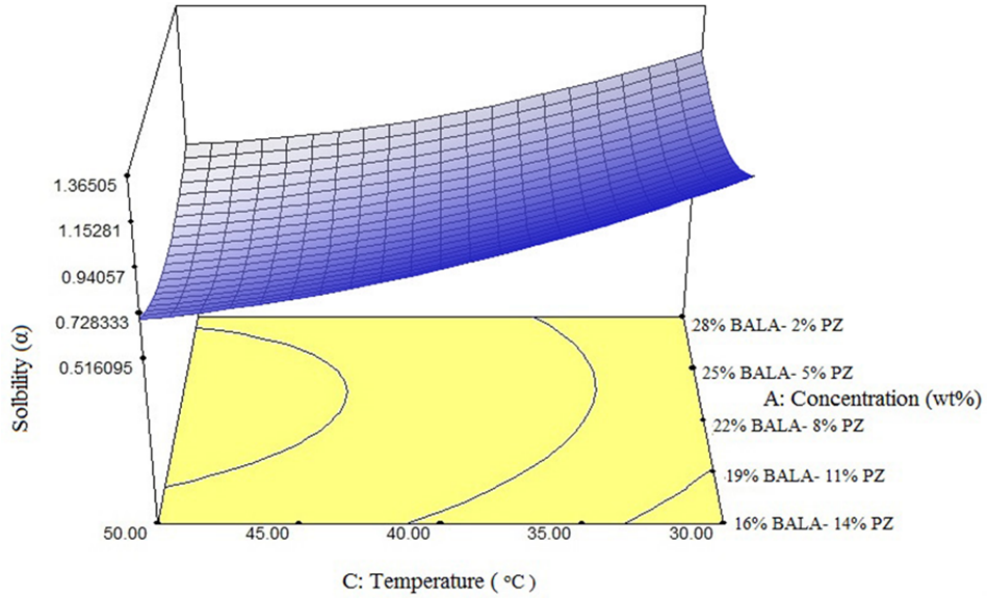


Fig. 6 Effect of temperature and concentration on solubility of CO_2 in aqueous solutions of (BA + PZ)

From the reported data of piperazine activated aqueous solution with β-Alanine, this hybrid solvent can be potentially effective to capture CO_2 from various process streams.

IV. Conclusion

The thermo-physicochemical properties of piperazine activated aqueous solution of B-alanine such as density, viscosity and solubility were experimentally measure and correlated. Density and viscosity values tend to decreases with increasing temperature.

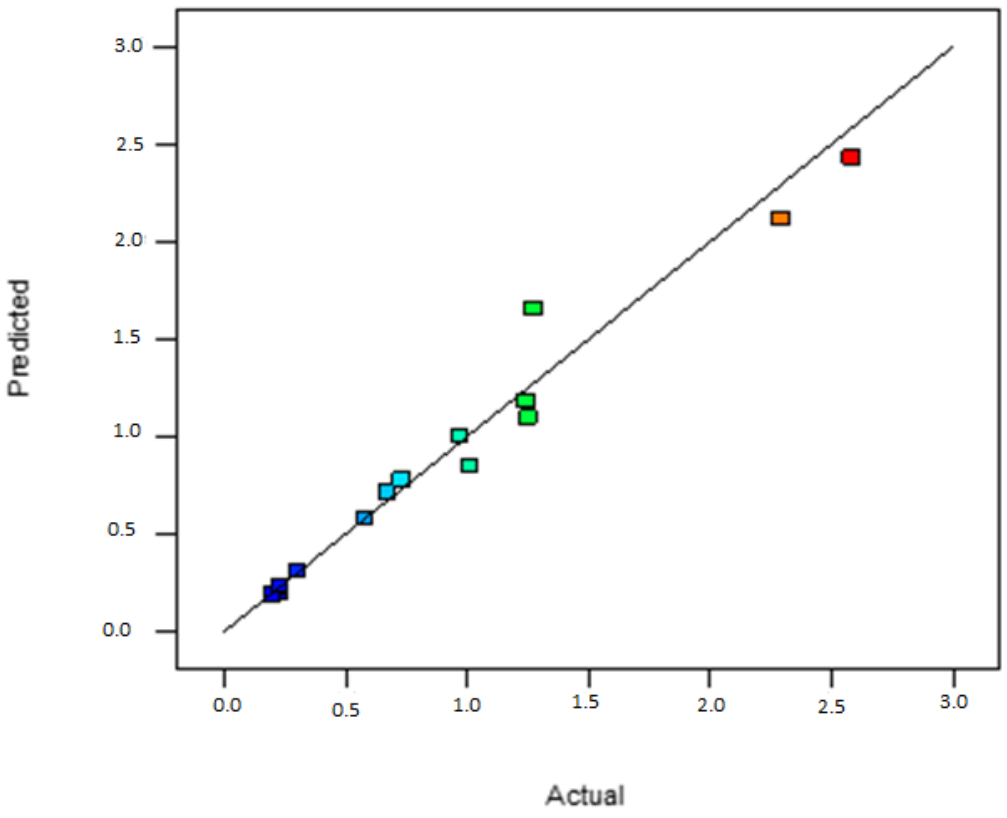


Fig. 7 Actual and model predicted values of solubility

Mathematical fitting equation of least square method was used to fit the experimental data and good agreement between calculated and measure values were found as reported in terms of standard deviations. Solubility of CO_2 in piperazine activated aqueous solution of B-alanine were measured over three important temperatures and up to maximum 10 bar pressure. It can be conclude that solubility increases with decreasing temperature and increasing pressure. Higher piperazine concentration in B-alanine solutions will contribute to high CO_2 loading capacity. The ANOVA analysis was also performed which to optimize the effect of the process variables. There was a good agreement found between predicted and actual solubility values. Piperazine activated aqueous solution of B-alanine can be a potential solvent to be used by the industry as an agent for CO_2 capture.

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