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Absorption Performance of CO₂ in p-Xylylenediamine Solution: Experimental Measurement and Modeling Using Response Surface Methodology

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INTRODUCTION

Rapid global development of the past hundred years has given rise to climate change as a major universal problem. The most important groups of solvents used in the absorption process are alkanolamines and ionic liquids, though the latter is rarely used because of high cost and viscosity [1]. An alternative modeling approach that is gaining popularity among researchers in this field and many other fields of science is the response surface methodology. This method allows the researcher to reduce the number of experiments thus the time and cost of research effort by designing the experiments [2].

The objective of this research was to introduce a new amine solution for CO₂ absorption. P-Xylylenediamine (PXDA) is a diamine consisting two primary amine groups, which can provide

good alkalinity for CO₂ absorption. Thanks to its high boiling point, this compound can be used for CO₂ removal at higher temperatures with minimum amine loss. To achieve the research objective, first, the solubility of CO₂ in PXDA solution was measured at PXDA concentrations of 2, 3.5, and 5mol/L, temperatures of 313-353 °K and pressures of 8-500 kPa. Next, the response surface methodology was used for modeling and analysis CO₂ solubility in this solution. In the end, CO₂ absorption rate, absorption capacity, cyclic capacity, and oxidation degradation of PXDA solution are compared with those of MEA, as one of the solutions is most frequently used in CO₂ removal applications.

EXPERIMENTAL PROCEDURE

CO₂ solubility and absorption rate are measured

by two cells made of stainless steel 316, both equipped with a thermocouple with accuracy of 0.1°K (model pt-100, fluda, germany) and two digital pressure transducer with 0-30 bar and 0-10 bar range (model PA-33X, Keller Druck) with the accuracy of (0.05%) kPa. In this work, CO₂ solubility is measured based on presented procedure in our previously published work [3].

MODELING

The software Design Expert (Stat-Ease; version 10.0.4) was used to process the data and investigate the effect of temperature, pressure, and PXDA concentration on CO₂ loading. To model the process, the experimental results were processed by analysis of variance (ANOVA) [4]. Table 1 presents the statistical analysis performed to examine the proposed model, and modified model used for modeling is given in Eq.1, where A, B, and C are concentration (mol/L), pressure (kPa), and temperature (°K) respectively.

Table 1: ANOVA results for the equations of the Design Expert for studied responses.

response	CO ₂ loading
P	0.0001>
CV	1.49%
R ²	0.9708
Adj.R ²	0.9631
Pred R ²	0.9519
AP	42.32

$$\begin{aligned}
 (\text{CO}_2 \text{ loading})^{2.32} = & 13.52 - 0.20 * A + 0.01 * B \\
 & - 0.071663 * C - 2.67615E - 004 * A * B + 1.25455E - \\
 & 003 * A * C - 1.85165E - 005 * B * C - 0.043051 * A^2 - \\
 & 2.51492E - 006 * B^2 + 9.49377E - 005 * C^2 \quad (1)
 \end{aligned}$$

RESULTS AND DISCUSSION

Fig. 1 shows the simultaneous effect of PXDA concentration and pressure on CO₂ loading at the tempera-

ture of 333 °K. As shown in the figure, as PXDA concentration increases, CO₂ loading decreases, and this decrease is almost irrespective of pressure. When PXDA concentration increases from 2 to about 3.5 mol/L, the reduction in CO₂ loading is relatively mild, but when it increases from 3.5 to about 5 mol/L, CO₂ loading decreases at a higher rate. From alternative perspective, an increase in pressure always corresponds to increase in CO₂ loading. However, pressure variations at lower pressure ranges have a greater effect on CO₂ loading. The simultaneous effect of temperature and pressure on CO₂ loading for PXDA concentration of 3.5 mol/L is illustrated in Fig. 2. As can be seen, higher temperatures generally lead to lower CO₂ loading. At low pressures, increase in temperature has limited impact on CO₂ loading, but at higher pressures, this effect is more pronounced. The simultaneous effects of temperature and PXDA concentration on CO₂ loading at the pressure of 275 kPa are plotted in Fig. 3. The effect of temperature on CO₂ loading is almost irrespective of PXDA concentration, and as temperature increases, CO₂ loading decreases at a relatively constant rate. Reduced CO₂ solubility at higher temperature is because of excess heat increases the kinetic energy of the molecules and breaks down the gas bonds, allowing the dissolved gas molecules with greater kinetic energy than solvent molecules to be released from the solution [5]. Another cause of decreased solubility at higher temperature is the exothermic nature of this process. Table 2 presents the net cyclic capacity values calculated for 2, 5 mol/L MEA and PXDA solutions to be used for absorption at the temperature of 313 °K and the pressure of 100 kPa and desorption at the temperature of 393 °K [3]. The high net cyclic capacity of PXDA as compared to MEA demonstrates the higher efficiency of this solution in CO₂ removal operation.

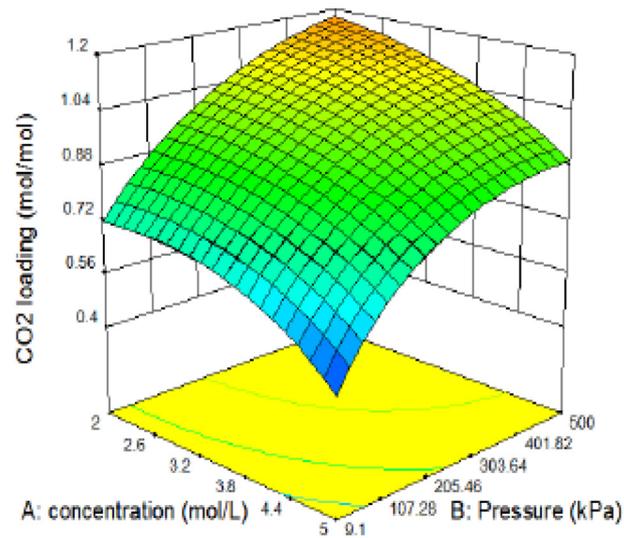


Figure 1: Response surface of CO₂ loading depending on concentration and pressure at T = 333° K.

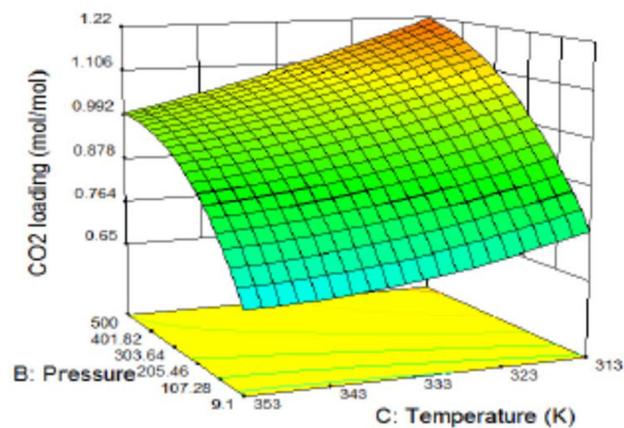


Figure 2: Response surface of CO₂ loading depending on Temperature and pressure at 3.5 mol/L.

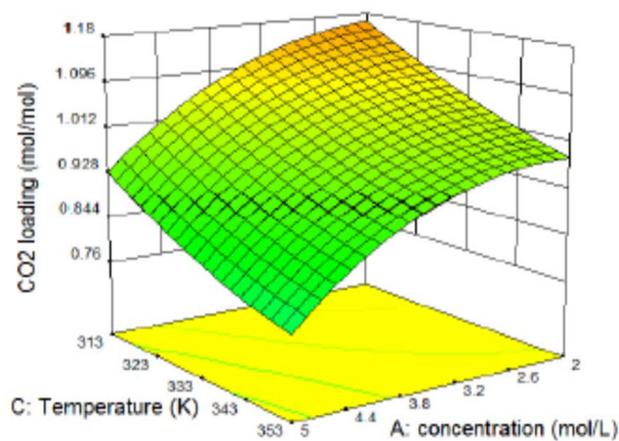


Figure 3: Response surface of CO₂ loading depending on concentration and temperature at p = 275 kPa.

Table 2: Net cyclic capacity PXDA and MEA, absorption at 313 °K and regeneration at 393 °K.

Solvent	Rich loading	Lean loading	Net Cyclic capacity
2M PXDA	1.025	0.392	1.266
5M PXDA	0.789	0.205	2.920
2M MEA	0.707	0.296	0.822
5M MEA	0.605	0.161	2.220

To investigate the effect of oxygen on the process, amine was exposed to pure oxygen at atmospheric pressure for 1 and 2 hours, and then CO₂ loading was measured according to the similar study [3]. After about 1 hour of exposure, CO₂ absorption of PXDA solution decreased by about 30% on average, while CO₂ absorption of MEA solution decreased by about 51%. After 2 hours, the reduction in CO₂ absorption reached to about 48% for PXDA solution and 67% for MEA solution. Therefore, it is clear that PXDA has a higher resistance to oxidative degradation than MEA.

In Fig. 4, CO₂ loading variations in PXDA solution with concentrations of 2 and 5M (mol/L) at the temperature of 313 °K, atmospheric pressure and in MEA solution with the same conditions are plotted versus time.

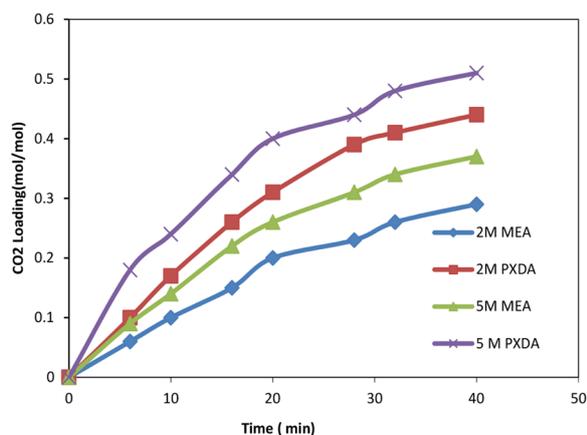


Figure 4: Experimental CO₂ loadings for aqueous solutions of 2, 5 M PXDA and MEA at 313°K versus time.

CONCLUSIONS

In this study, PXDA was introduced as a new amine for CO₂ absorption. CO₂ absorption was performed in a bath reactor at the temperatures of 313 °K, 333 °K, and 353 °K, pressures of 8-500 kPa, and solution concentrations of 2, 3.5, and 5 mol/L. Moreover, the response surface methodology was used to examine the parameters influencing the CO₂ loading of amine solution. In addition, the results of ANOVA confirmed the accuracy of the model. The results obtained from the experiments at concentrations of 2 and 5 mol/L, pressure of 100 kPa, and temperature of 313 °K showed that PXDA solution has a 45% higher absorption capacity and 44% higher absorption rate than MEA.

The mean oxidative degradation of PXDA after 1 and 2 hours of oxidation at different pressures was respectively 30% and 48%, but for MEA, those values were 51% and 67%, respectively. With pressure set to 101.325 kpa (atmospheric pressure), absorption temperature set to 313 °K, and desorption temperature set to 393 °K, the net cyclic capacity of PXDA is greater than MEA solution. As a result, it can be claimed that PXDA solution has a much better CO₂ capture performance than the typical industrial solution that is MEA.

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