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Research Paper

Experimental and theoretical study of CO_2 absorption by Water-Ionic liquid-Piperazine solution using the method of Constrained Mixture Design

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1. ABSTRACT

Carbon dioxide gas is one of the most common environmental pollutants that can cause a lot of damage. Separation of carbon dioxide gas from natural gas flow using amine mixture is one of the most common methods. In this research, the optimal composition of the amine mixture was determined using the method of designing limit vertices. The amine mixture used in this research included water, piperazine and 1-butyl-3-methylimidazolium hydrogen sulfate. In order to measure the solubility of carbon dioxide in amine solution, an equilibrium cell (autoclave) was used. According to analysis of variance, explanation coefficient (R2) has a high value (R2=99.79%). The analysis of the results was done at the 95% confidence level in a block with the number of 9 tests and Ludinig's definition as the response variable. The optimization results showed that the combination consisting of 811.24 ml of water, 188 ml of amine and 0.76 ml of ionic liquid had the best efficiency and in this case the maximum loading of 1.702 was obtained.

Keywords: Carbon dioxide; Piperazine; Ionic liquid; Vapor-liquid equilibrium

2. INTRODUCTION

One of the most essential human needs is the need for clean air. Population growth and human industrial activities after the industrial revolution have caused an increase in the consumption of fossil fuels. Combustion of fossil fuels introduces a huge amount of gaseous pollutants into the environment. The main part of greenhouse gases is carbon dioxide, which is not a poisonous gas, but its increase in the long term causes global warming [1]. Due to the dependence of the world economy on fossil fuels and since the combustion of these fuels is the most important source of CO_2 gas production, this gas is considered as the most important greenhouse gas, which is about 68%. It accounts for the total emission of greenhouse gases. Therefore, controlling the amount of CO_2 in the atmosphere is very important in protecting the environment [2]. Studies show that carbon dioxide comprises about 75-80% of greenhouse gases in Iran. The research conducted in the field of carbon absorption until today has led to the presentation of four technologies, including surface absorption, membrane separation, refrigeration and physico-chemical absorption with solvent for the separation of carbon dioxide. Among the mentioned methods, the process of reactive absorption with chemical solvents such as aqueous solution of alkanolamines has been found and used in industrial terms, technically and economically justified. Recently, aqueous solutions of diamines such as piperazine have attracted the attention of scientists due to their high reaction rate with CO_2. Diamines have a greater capacity to absorb CO_2 than monoamines, and at high partial pressures of CO_2, each mole of piperazine can absorb more than 3 moles of CO_2. In 2021, Lee et all investigated the absorption of CO_2 with amine piperazine and 1-methyl piperazine solutions. They reported the amount of CO_2 absorption by these solutions as 99.3% [3]. In this research, the theoretical and experimental effects of amine mixture including water, piperazine, 1-butyl-3-methylimidazolium hydrogen sulfate and ionic liquids on the solubility of carbon dioxide gas will be determined. Therefore, the main goal of this research is to provide the most suitable and optimal amino compound for removing carbon dioxide. Since carbon dioxide separation processes have become very wide and diverse, therefore, modeling of such processes is of particular importance, because using modeling in the development of a process is much more economical

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than conducting costly experiments. In order to design the process equipment of gas purification units, vapor-liquid equilibrium information is needed. Therefore, in this research, in order to model and prevent repetition of experiments and save costs, determining the optimal composition of carbon dioxide in an aqueous solution of piperazine-ionic liquid was done using modeling of the constrained mixture design.

3. MATERIALS AND METHODS

All the materials used were of high purity and were used without further concentration or purification. Deionized water (obtained from Sina Company, Iran), sulfuric acid, hydrochloric acid, nitric acid, piperazine (obtained from Sigma Aldrich with a purity of 90.99), nitrogen gas (purchased from Shimiran Company), sodium hydroxide, 1-Butyl 3-methylimidazolium hydrogen sulfate (produced by Merck with 99% purity), sodium chloride and potassium chloride (produced by Merck with 99.90% purity) were used. By having the initial temperature and pressure of the reactor, the initial number of moles of gas entered into the reactor, and by determining the final temperature and pressure, the number of absorbed moles of gas was obtained using the ideal gas state equation. The duration of each test depends on the speed of solvent absorption. Using the ideal gas law, and having the inlet temperature and pressure values, the number of moles of carbon dioxide at the beginning of the process (n_1) is calculated using equation (1).

$$n = \frac{PV}{RT} \tag{1}$$

The number of moles of gas after the process (n2) is measured again using equation (1). The number of moles of carbon dioxide absorbed by the amine mixture is the difference between these two values, which is calculated from equation (2).

$$n = n_1 - n_2 \tag{2}$$

4. RESULTS AND DISCUSSION

4.1. Subtitle

To determine the appropriate composition of the mixture, considering the sum of 1000 for the volumetric composition of the three components, the mixture test design method is used [4]. In this research, water volume (V_1), piperazine volume (V_2) and ionic liquid volume (V_3) are considered as independent variables:

$$\mathbf{V_1 + V_2 + V_3 = 1000} \tag{3}$$

Table 1. The range of variables considered in mixed experimental design

variable	abbreviation	Range
Volume percentage of water	V_1	$750 \le V_2 \le 900$
Volume percentage of piperazine	V_2	$99 \le V_2 \le 200$
Volume percentage of ionic liquids	V_3	$0 \le V_3 \le 1$

Loading was determined as the response variable, which is calculated from equation (2).

$$\text{Loading} = \frac{\text{adsorbed carbon oxide dimol number}}{\text{amine mole number}} \tag{2}$$

The constrained mixture design experiment to determine the optimal composition of the amine mixture, the analysis of the results at the 95% confidence level was carried out in a block with the number of 9 experiments and the definition of Ludinig as the response variable [5]. The test results are shown in Table 2.

Table 2. Design results of the simple center of gravity test to find the optimal composition of the amine mixture

Test	Water (mL)	Amine (mL)	Ionic liquid (mL)	loading
1	799.90	200.000	0.100	1.12
2	874.30	124.925	0.775	1.31
3	824.70	174.975	0.325	1.22
4	799.00	200.000	1.000	1.44
5	824.25	174.975	0.775	1.54
6	849.50	149.950	0.550	1.43
7	899.10	99.900	1.000	1.30
8	874.75	124.925	0.325	1.14
9	900.00	99.900	0.100	1.02

4.2. Optimizing and choosing the optimal combination

Contour diagrams and three-dimensional drawing of parameters are presented in Figures 1 and 2.

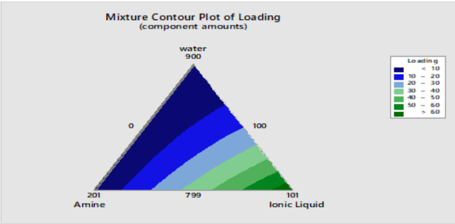

Figure 1. Triangular contour for drawing boundary vertices

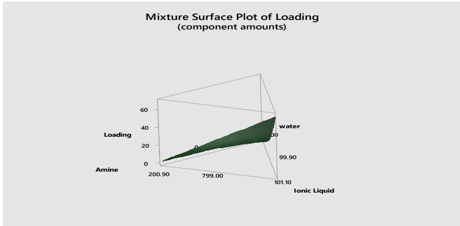

Figure 2. 3D-contour diagram for drawing boundary vertices

In Fig. 1, at each vertex of the triangle, one of the parameters is at the level of its maximum value. The side of the triangle is a mixture of two parts that are located at the two ends of the side. In the range of the triangle, depending on which section the selected point is located, the composition ratio of the components changes. The response variable has the lowest value in the blue range and the highest value in the bold green range.

Optimization was done by defining a utility function, with the approach of maximizing the response rate in Minitab software. The results obtained are listed in Table 3.

Table 3. Optimal levels of the Constrained Mixture Design test design

volume of water	amine volume (mL)	ionic liquid volume (mL)	Loading
811.24	188	0.76	1.702

According to Table 3, the optimization results by the software show that the combination consisting of 24.811 ml of water, 188 ml of amine and 0.76 ml of ionic liquid has the highest efficiency and in this case the maximum loading is 1.702.

5. CONCLUSION

In this research, the effect of the combination of amine mixture and ionic liquids on the solubility of carbon dioxide gas in the amine composition and the behavior of this system was investigated. The most important results obtained are: The optimal composition of the amine mixture was determined using the design of three-level vertices with the number of 9 experiments, and in this study, it was determined that the optimal composition included 811.24 mL of water, 188 mL of piperazine, and 76.7 mL of water. The ionic liquid is 1-butyl-3-methylimidazolium hydrogen sulfate. The mixed design model was determined to be sufficient by analysis of variance and had a good agreement (R^2=99.79%) with the data obtained from the experiment. According to the experiences obtained from this research, the continuation of the experiments of this research with other alkanolamines such as diglycolamine, the modeling of CO_2 gas solubility data using thermodynamic models, such as Kent-Eisenberg, and the use of ionic liquids based on pyridinium and ammonium for future researches. Which takes place in a similar context, is recommended.

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