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DIFFUSION COEFFICIENT IN EMULSION CONTAINING MONOETHANOLAMINE AND 2-AMINO-2-METHYL-1-PROPANOL.

Z.M. Ibrahim*, K.S.N. Kamarudin

Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, Skudai, Johor Bahru.
**Corresponding Author Email: zulaikha7@live.utm.my*

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ABSTRACT

In industry, the removal of carbon dioxide is very important because of the optimization of the capital and the operation cost of a process, to meet the specification of the gas and for environmental purpose. The absorption technique to capture carbon dioxide is widely used in gas separation in industry. The most common technique that usually used is absorption using alkanolamines. Recent technology regarding separation of gas by using emulsion has been studied which using amine as extractant and organic solvent. However, during the absorption process, the unknown value of diffusivity coefficient causes the amount of carbon dioxide diffuse pass through the emulsion layer cannot be estimated. The viscosity and time of absorption needs to be considered in this study. In this study, the materials used were methylethanolamine (MEA) as a stripping agent, 2-amino-2- methyl-1-propanol (AMP) as activator and sodium hydroxide (NaOH) solution as an aqueous phase together with an organic phase consist of kerosene and Span-80. The concentration of MEA/AMP and Span-80 were varied to determine the viscosity and the diffusivity coefficient of the CO2 in emulsion during absorption. Diffusion coefficient was calculated based on the equation by using Wilke-Chang theory. Rotating disc contactor (RDC) was used and the amount of CO2 was measured by using gas chromatography (GC). This study showed that, using 8 mL MEA and 4mL AMP, the diffusivity coefficient and amount of CO2 absorbed were 14.23 x 10-8 and 963.31 mmol of CO2 respectively.

KEYWORDS

carbon dioxide, methylethanolamine (MEA), 2-amino-2- methyl-1-propanol (AMP), sodium hydroxide (NaOH), Rotating disc contactor (RDC), gas chromatography (GC).

1. INTRODUCTION

A study on carbon dioxide removal has been increased to solve the problem regarding to global warming which is getting worst. Based on a study, the temperature rising would eventually lead to the increase in sea level, if it cannot be controlled, it may cause the occurrence of storms and floods [1].

The absorption process is the most common process that has been used in the industry to remove carbon dioxide. Other than absorption, there are a few other methods to remove carbon dioxide which are adsorption, cryogenic process and by using membrane. The common process that always been used in the industry is absorption by using alkanolamines such as methyldiethanolamine (MDEA), monoethanolamine (MEA) and diethanolamine (DEA). The improvement of the study regarding to the use of alkanolamines also has been done by using combined amine such as MEA/AMP which MEA as stripping agent and AMP as activator. According to research, alkanolamine-based aqueous solutions are frequently used for CO2 chemical absorption due to their high reactivity with CO2 [2]. Separation of CO2 gas by using absorption in emulsion technology has been studied recently. Emulsion gives high simultaneous purification and concentration of the solute because of combination of extraction and stripping process. The absorption mechanism of CO2 into emulsion composed of aqueous amine solution (MEA, DEA, TEA) and organic solvent which CO2 passes through organic solvent through the gas-liquid interface under unsteady state transfer into the dispersed aqueous droplets through liquid-liquid interface under steady state.

The MEA is a primary amine and is the most commercially significant amine as it reacts fast and efficiently. AMP is the most characteristic amine of a special category of amines called sterically hindered amines (SHA) which form more unstable carbamates in comparison with other amines. SHA have been known to exhibit a high loading with a high absorption rate.

The study of diffusion is very important to understand the molecular motion and interactions in the dense fluids. It is the main parameter in separation process, tertiary-oil recovery and the extraction of essential oils from vegetable matrices. It can also be used to estimate infinite dilution of binary mass diffusion coefficient in the thermodynamic researching field or to model and design the industrial mass transfer operations. Although the empirical models have been widely used to predict gas solute diffusivity in water and simple solvents, their applicability and accuracy in predicting gas diffusion coefficient in liquid has yet to be systematically examined [3].

Gan and his partners have given an extensive review of the methods to calculate diffusion coefficient for gas in supported ionic liquid membrane. According to Einstein's equation, the diffusion coefficient of solutes in liquid is directly proportional to the reciprocal of the molecular radius of the diffusing solute. Wilke-Chang theory of diffusion is considering molecular interactions and properties of both diffusing molecule and the liquid media diffusion. The correlation of Sheibel was modified from Wilke-Chang theory to eliminate the association factor. The measured of diffusivity in Gan and his coworkers studied by mentioned correlation are applied to analyze gas permeation and separation through supported ionic liquids by the conventional solution-diffusion theory.

Previous study regarding to gas-liquid diffusion coefficient has been discovered thoroughly in the emulsion. Several methods which are experimental measurement, theoretical calculation and dynamics simulation are used to obtain the gas diffusion coefficients. However, the accuracy and condition of experimental measurement is limited to certain temperature and pressure that make the data is inconvenient for engineering application.

The accuracy of theoretical calculation can be relatively satisfied but there is no well-established theoretical calculation for diffusivity coefficient of CO_2 absorption in the emulsion. The removal of CO_2 involves diffusion through a thin layer of membrane that separates the organic phase from the aqueous phase. The thickness of the thin layer also depends on the type of surfactant used.

The objectives of this study were to determine diffusivity coefficient of CO_2 in different concentration of MEA/AMP mixture and different concentration of Span-80 and to observe the correlation between the amount of CO_2 and calculated diffusivity coefficient.

To achieve objectives, the concentration of MEA/AMP was varied and the different in concentration of Span-80 was used for the preparation of emulsion. The viscosity was determined, and the diffusion coefficient was calculated based on suitable Wilke-Chang theory. The experimental measurement was conducted by using rotating disk contactor (RDC) and the absorption amount of CO_2 was correlated with calculated value of diffusivity coefficient.

2. EXPERIMENTAL

2.1 Preparation of Emulsion

For the preparation of aqueous phase, MEA, AMP and NaOH were used. MEA/AMP were mixed and stirred and were added into 0.1M NaOH solution to prepare 100 mL of aqueous phase. The mixture was stirred for 5 minutes. Kerosene and Span-80 were used for preparation of organic phase. For aqueous and organic phase of stirring speed and temperature of the heating plate, they were fixed at 700 rpm and 27°C respectively.

The high-performance disperser Ultra Turrax® with 18G mixing shaft was used in the preparation of emulsion. 100 mL of organic phase mixture was placed in the beaker and 100 mL of aqueous phase was placed into the beaker containing organic phase, drop by drop and homogenized to produce water-in-oil emulsion. The formulation of emulsion was shown in Table 1.

Table 1: Preparation of Emulsion by Varied AMP.

Aqueous Phase			Organic Phase	
MEA (%v/v)	AMP (%v/v)	NaOH (%v/v)	Span-80 (%v/v)	Kerosene (%v/v)
8	0	92	8	92
8	2	90	8	92
8	4	88	8	92
8	6	86	8	92
8	8	84	8	92

To determine the effect of AMP with 8% v/v of MEA, different concentration of AMP was used from 0% v/v until 8% v/v. In this study, the different concentration of Span-80 was also used between 2% v/v, 4% v/v and 8% v/v to identify the effect of Span-80 on the diffusivity of CO_2 in absorption of emulsion. The homogenization of different aqueous phase and organic phase were at 10 000 rpm and 5 minutes' emulsification speed and time. The best formulation (MEA/AMP and Span-80 concentration) was based on diffusivity coefficient of emulsion and the amount of CO_2 absorbed.

2.2 Measurement of Viscosity

Measurement of the viscosity of the aqueous phases and organic phases was conducted by using Programmable Rheometer Brookfield Model DV-III at room temperature. The measurement of the viscosity of emulsion was to estimate the diffusivity of CO_2 in the emulsion. A spindle (type 00) was used at a motor speed of 60 rpm.

2.3 Diffusion Coefficient

The diffusivity coefficient of the emulsion was determined by using Wilke-Chang theory which was widely used as empirical correlations to estimate gas diffusion coefficients in liquids which take consideration of molecular interactions and properties of diffusing molecule and diffusion liquid.

$$D = (7.48 \times 10^{-8}) \frac{T\sqrt{\alpha M_2}}{\mu V^{0.6}} \qquad (1)$$

Where, D is the diffusion coefficient (m^2/s), α is the association constant which accounts for gas-liquid interactions (0.15), V is the molar volume of gas solute at it boiling point (cm^3/mol), μ is the solution viscosity (mPa s). T refers the temperature (K) and M_2 is the molecular weight of the solvent (g/mol).

2.4 Absorption of Carbon Dioxide

Rotating Disc Contactor (RDC) used has been modified by enlarging the axially rotating disc based on the gas-liquid parameters, gas-liquid flow behavior, retention time and mass transfer. The modification of RDC resulted to have larger surface area for absorption between the emulsion and the gas feed. Furthermore, the function of new modified RDC was to maintain homogeneity of the emulsion in the column. According to research, RDC can prolonged the duration of the gas inside the RDC thus the longer contact time can be achieved [4-6].

To determine the amount of carbon dioxide absorbed in the prepared emulsion, Gas Chromatography (GC) was connected to the rotating disc contactor. The calibration of GC was focused on CO_2 gas measurement. The flowrate of CO_2 gas used was 20 LPM (Litre per minute). The retention time and peak of CO_2 gases was identified. 200 mL of prepared emulsion was poured into the RDC and the stirrer speed was at 500 rpm. Then, CO_2 gas was fed into the RDC for 10 minutes. 10 minutes absorption time at 10 minutes was the optimum time for carbon dioxide absorption [7]. The inside pressure of the RDC was recorded. The gas supply was stopped after 10 minute and the measurement by using GC started. The amount of CO_2 gas absorbed was calculated.

3. RESULTS AND DISCUSSION

3.1 Viscosity of Emulsion

The viscosity play an important role to provide an information on emulsification. This is because, during emulsification, small particles that have far distance between each other, take longer time to settle down. If the solution has too high in viscosity, it will reduce the dispersion in aqueous phase thus will reduce the absorption of CO_2 gas.

In this study, the viscosity emulsion was determined. The formulation of membrane phase and the condition during emulsion preparation was observed to determine effect to the emulsion viscosity. Najib et. al7 found that high viscosity was caused by the larger droplets of emulsion. Concentration of MEA/AMP and Span-80 in emulsion may influenced the characteristic of emulsion [8].

The viscosity of emulsions is related to amine contain where AMP (147 cP) has a higher viscosity as compared to MEA (24.085 cP) The emulsion viscosity will be higher when the concentration of AMP increases [9]. Table 1 shows the formulation used and the condition of MEA/AMP mixture where the emulsification time and it speed at 5 minutes and 10 000 rpm respectively. As shown in Figure 1, viscosity shows an unstable result. When the concentration of AMP at 4% v/v to 6% v/v shows that it increased in viscosity and during concentration at 8% v/v, the viscosity slightly decreased.

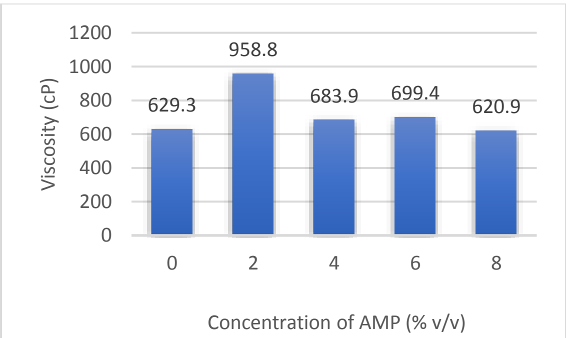

Figure 1: The viscosity of emulsion at different concentration of AMP

Table 2 shows the formulation and condition during emulsion preparation for different concentration of Span-80. Span-80 was used as a surfactant because hydrophile-lipophile balance (HLB) value of Span-80 is 4.3 that tend to form water-in-oil emulsion. Other than that, Span-80 indicates the effect of surfactant on the diffusivity of carbon dioxide in the emulsion. The viscosity of the different concentration of Span-80 was measured as shown in Figure 2. The viscosity of the emulsion was increased when the higher concentration of Span-80 was used in the experiment.

Table 2: Formulation and condition used for removal of carbon dioxide at variation Span-80 concentration.

Formulation/Condition	Specification
MEA: AMP: NaOH	8% v/v: 4% v/v: 88% v/v
Kerosene: Span-80 (100 mL aqueous phase)	i. 98% v/v: 2% v/v ii. 96% v/v: 4% v/v iii. 92% v/v: 8% v/v
Emulsification Speed	10 000 rpm
Emulsification Time	5 minutes

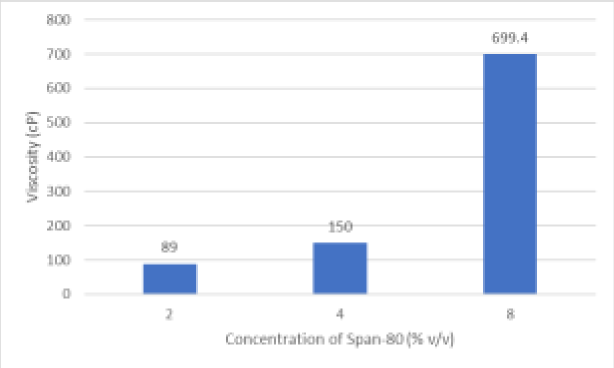

Figure 2: Viscosity of emulsion with different concentration of Span-80.

3.2 Diffusion Coefficient

In this study, the diffusivity coefficient of CO2 during diffusion through emulsion was calculated by using Wilke Chang theory1. The increase of viscosity in emulsion was resorted to decrease in diffusion coefficient of carbon dioxide, based on Equation (1) (Wilke-Chang diffusion coefficient correlation). Figure 3 shows relationship between viscosity and diffusivity coefficient with different concentration of AMP.

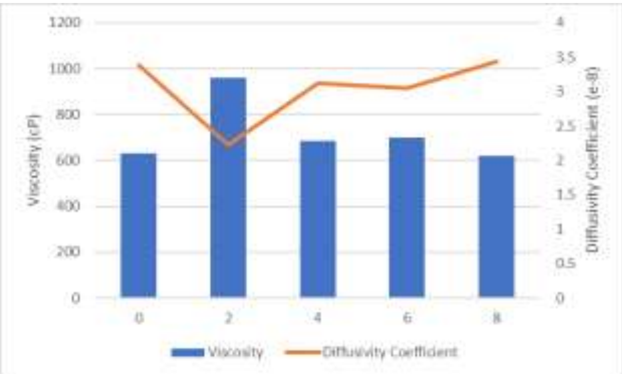

Figure 3: Relationship viscosity and diffusivity coefficient with different concentration of AMP.

This study showed the effect of different concentration of AMP on the diffusivity of carbon dioxide. Sreedhar and his coworkers discovered that the increase of concentration of AMP in the aqueous phase was resulted to the higher of absorption of carbon dioxide. This is because, AMP has good absorption capacity, degradation and corrosion resistance, lower energy penalties and higher selectivity.

The high viscosity was observed to have an effect to the diffusivity of carbon dioxide during the absorption process, thus lead to decrease in diffusivity of carbon dioxide (Figure 4). This is because, when larger droplet of emulsion form, the viscosity of that emulsion increases the resistance of the carbon dioxide to be absorbed into the emulsion droplet. This is because the viscosity may cause the surfactant surface to hold the emulsion droplets thus it is difficult for carbon dioxide to absorb through interface.

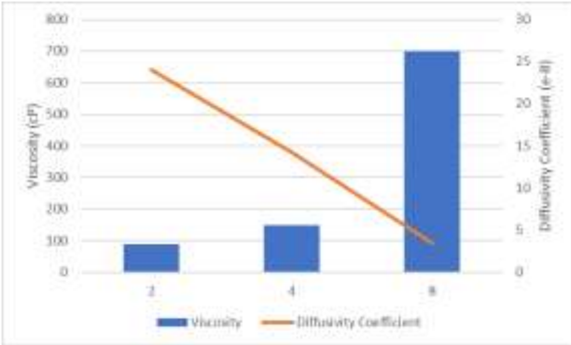

Figure 4: Viscosity and diffusivity coefficient of different concentration of Span-80.

Eventually, the viscosity of the emulsion liquid membrane was affected by both amine and Span-80. As shown in Figure 4, the emulsion formulation that has higher CO2 absorption of when Span-80 concentration at 2% v/v. Increased in diffusion coefficient was expected to have higher absorption of CO2.

3.3 CO2 Absorption

Absorption of CO2 emulsion conducted in Rotating Disc Contactor system. The amount of carbon dioxide absorbed was determined from Gas Chromatography. The absorption rate of gas into the emulsion was controlled by gas diffusion in the aqueous phase. Table 3 shows the formulation and condition of CO2 absorption of the at different concentration of AMP.

Table 3: Formulation and condition of absorption of CO2 at different concentration of AMP.

Formulation/Condition	Specification
MEA: AMP: NaOH	i. 8% v/v: 0% v/v: 92% v/v ii. 8% v/v: 2% v/v: 90% v/v iii. 8% v/v: 4% v/v: 88% v/v iv. 8% v/v: 6% v/v: 86% v/v v. 8% v/v: 8% v/v: 84% v/v
Kerosene: Span-80 (100 mL aqueous phase)	92% v/v: 8% v/v
Emulsification Speed	10 000 rpm
Emulsification Time	5 minutes
Agitation Speed	500 rpm
Absorption Time	10 minutes

The amount of CO2 absorbed through the emulsion was shown in Figure 5. From the graph, the highest amount of CO2 was absorbed at 8% v/v of AMP concentration. The comparison was made between calculated diffusivity coefficient and the amount of CO2 absorbed. Based on that, when the diffusivity coefficient higher, the amount of CO2 absorbed also increased. As shown in Figure 3, the diffusion coefficient at 8% v/v AMP concentration were 3.13 x 10-8 cP, which resulted to have higher in amount of CO2 absorbed (446.377 mmol).

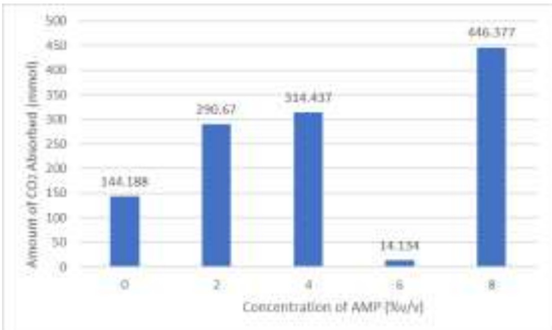

Figure 5: Amount of carbon dioxide absorbed in emulsion with different concentration of AMP.

As shown in Table 4, the formulation and condition during absorption of CO_2 at different concentration of Span-80. The best formulation of concentration of AMP for aqueous phase was chosen which was 4% v/v of AMP concentration. The result, as shown in Figure 4. The highest amount of absorption of CO_2 was at 4% v/v of Span-80 concentration. Najib and her partner found that as more Span-80 was added, the viscosity of emulsion was also increased thus will lower the amount of the carbon dioxide being absorbed. The increased in viscosity significantly will decrease the diffusivity for Newtonian fluids.6 Thus, increased of viscosity resulted in decreased the diffusivity coefficient of the carbon dioxide and eventually decreased the amount of CO_2 absorbed. As for the favourable formulation, the concentration of Span-80 at 4% v/v was the best formulation that absorbed.

Table 4: Formulation and condition of absorption of CO_2 at different concentration of Span-80.

Formulation/Condition	Specification
MEA: AMP: NaOH	8% v/v: 4% v/v: 88% v/v
Kerosene: Span-80 (100 mL aqueous phase)	i. 98% v/v: 2% v/v ii. 96% v/v: 4% v/v iii. 92% v/v: 8% v/v
Emulsification Speed	10 000 rpm
Emulsification Time	5 minutes
Agitation Speed	500 rpm
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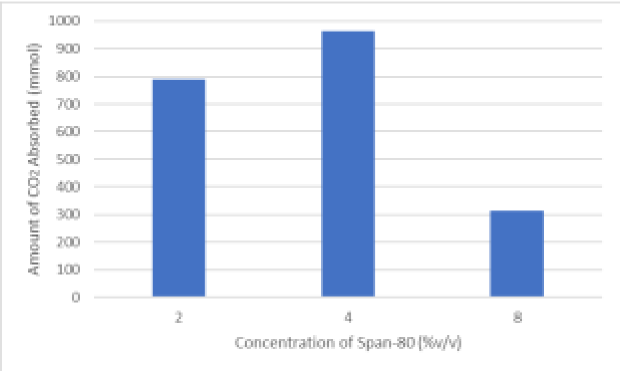

Figure 6: Amount of carbon dioxide absorbed in emulsion with different concentration of Span-80.

4. CONCLUSION

In conclusion, the different concentration of MEA/AMP mixture and Span-80 were gave an impact towards diffusivity coefficient by having different viscosity of emulsion. The increased in viscosity decreased the value of diffusivity coefficient. However, the increased in diffusivity coefficient will increased the amount of CO_2 absorbed in emulsion. The favorable formula was chosen is 8% v/v MEA and 4% v/v AMP which the diffusivity coefficient and amount of CO_2 absorbed were 14.23 x 10-8 and 963.31 mmol of CO_2 respectively.

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