THE EFFECT OF COSURFACTANT IN CO_2 ABSORPTION IN WATER – IN – OIL EMULSION

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ARTICLE DETAILS

ABSTRACT

Carbon dioxide is one of the main concern in the environment when it comes to energy usage of fuel, even the fuel is coming from natural gas sources. Apart from endangered the environment, carbon dioxide also affects the caloric value of the natural gas itself. The presence of carbon dioxide as contaminants is a nuisance for oil and gas industry as its capability of forming corrosion in pipeline, thus its removal is vital for this industry. The absorption of carbon dioxide in emulsions would be an effective method to prevent corrosion. This study focused on the effects of cosurfactant, complementing 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) with surfactant which is sorbitan oleate (SPAN 80), on the stability of water-in-oil (W/O) emulsion. This study also investigates the use of blended amines which are methyldiethanolamine (MDEA)/2-amino-2-methyl-1-propanol (AMP) and MDEA as aqueous phase. A modified rotating disk contactor (RDC) was used in absorption process and gas chromatography (GC) was used to determine the amount of the CO2 absorbed. Analysis of carbon dioxide absorption through emulsion indicates that different cosurfactant may change the absorption mechanism.

KEYWORDS

1. INTRODUCTION

The usage of fossil fuel as a source of energy for worldwide has made an impact to environment. This is due to burning of fossil fuel and releasing a large amounts of carbon dioxide produced annually in various industries. Natural gas that contains carbon dioxide and hydrogen sulphide is called "acid gas". A process of removal of certain undesirable contaminants such as sulphur containing compounds, carbon dioxide, mercury, from processed hydrocarbon is known as gas sweetening. A number of methods are available for removal of acid gases from product streams. Some of the more commonly used method are physical absorption, chemical absorption, adsorption and membrane separation, among them physical and chemical absorption methods have more industrial importance [1].

There are several consecutive steps for chemical absorption of gas in a liquid phase which contains: (1) penetration of gas in the gas towards the gas-liquid interface, (2) physical dissolution of gas in the liquid phase, (3) diffusion in the liquid bulk of dissolved gas, and (4) chemical reaction between the dissolved gas and a reactant in the liquid phase [1-3]. It can be said that the physical dissolution in the liquid phase may control the gas absorption rate due to fast chemical reaction between gas and the reactant in the liquid phase. The rate of absorption can also be improving by increasing the contact surface area between the gas and liquid phases using small drops of liquids in the approach of emulsion.

The theory in the absorption of carbon dioxide in emulsion is that, since the chemical reaction between the gas and the reactant in the liquid phase is spontaneous (and may be fast depending on the reactant type), the other following steps in the chemical absorption process is a diffusion of gas through the gas and the liquid boundary layers, and gas diffusion in the liquid phase control the absorption rate. Therefore, measures the gas dissolving in the liquid, can enhance the rate and capacity of gas absorption in the liquid phase. Thus, to increase the interfacial area in the mass transfer path is by introducing tiny liquid droplets of reactive phase into another liquid phase, i.e. applying an emulsion in contact with the gas phase.

Emulsion may provide a large interfacial area between the continuous and the dispersed liquid phases where the gas will dissolve physically from the gas phase into continuous phase, and then transfer to the dispersed reactive phase to react with the reactive component. On the other hand, applying a W/O emulsion can provide a thin film on the absorption equipment and may slacken the corrosion phenomenon where, often observed when amine is used as solvent [1]. Emulsion stability is affected mainly by surfactant, thus with correct formulation of surfactant, the rate of gas absorption in liquid phase can be investigated. In this study, the absorption of CO_2 in W/O emulsion will focus on the effect of surfactant in the stability of emulsion and the rate of removal of CO_2.

CO_2 removal is vital for natural gas before it is release as a product to sale to customer. From previous studies it is shown that absorption of CO_2 in emulsion is an effective method to prevent corrosion. However, it is important to maintain the stability of the emulsion which depends on the type and the quantity of surfactants. Unstable emulsion or demulsifications reduces the absorption rates thus reduces its ability to prevent corrosion because amines may directly in contact with the metal surfaces.

Suitable formulation will produce stable emulsion with high efficiency of the separation. It was reported that surfactant plays and important role during the absorption because excessive stability of emulsion reduced the efficiency of separation process [4]. Previous studies showed that the problem arise as CH_4 was also absorbed together with CO_2 during the absorption process. Therefore, a new formulation using different type of surfactant need to be identified in order to produce stable emulsion with high percentage of separation.

The selection of surfactant was based on the HLB number, which the value is less than 5 and non-ionic surfactant such as Span 80 are able to stabilize W/O emulsions [5,6]. The method of W/O emulsion preparation using

Span 80 has been widely used by previous studies [5]. Two different types of aqueous phase were used, there were the combination of MDEA/AMP and MDEA only. For MDEA/AMP, 8% v/v MDEA and 88% NaOH and 4% v/v AMP and for MDEA, 8% v/v MDEA was the best for CO_2 absorption [7]. Despite the appealing features of emulsion, this technique used in absorption is not widespread used due to the instability of emulsion [8]. Thus, this study suggesting forming an adhesive emulsion that could stabilize the emulsion based on experiment conducted by some researchers [6]. A stable adhesive emulsion using DOPC as surfactant and the cosurfactant the molecular structure complementary to DOPC was Span 80 and DHA. This study applied the preparation technique to produce a stable emulsion as a medium for separation of CO_2 gas.

In this study, adhesive emulsion was introduced in the separation process where the particles of the adhesive components are equal in size with emulsion components (the liquid vehicle for carrier throughout which the adhesive components are dispersed). This feature will give the adhesive a continuous surface and creates stronger initial and ultimate adhesion (as there is a larger surface area over which the adhesive bond can form) [6]. Adhesive emulsion was considered in this study to evaluate the separation process of CO_2 from gas mixture. This adhesive emulsion was stabilized by 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) which typically unstable because of its molecular structure.

Previous study showed that with low stability of emulsion, it will affect the separation process [9]. To achieve a stable adhesive water-in-oil emulsion, a cosurfactant was added and identified as Span 80. With addition of cosurfactant whose molecular shapes could be complementary to that of DOPC thus far better stabilizes W/O emulsions and was applied in CO_2 separation. Thus, the focus is to formulate a stable emulsion using DOPC with cosurfactant, Span 80 and to investigate the percentage of absorption of CO_2 gas using adhesive emulsion.

2. EXPERIMENTAL

2.1 Materials

Emulsion was formed by homogenizing the aqueous and organic phase. For the aqueous phase, a combination of blended amines were used, MDEA/AMP and MDEA. Sodium hydroxide (NaOH) pellets were dissolved in water to form sodium hydroxide solution for the aqueous phase. Organic phase consists of DOPC with SPAN 80 to form a cosurfactant, are used in the formulation while the diluent used was kerosene.

2.2 Emulsion Preparation and Observation

To prepare the aqueous phase, MDEA and AMP was mixed in a beaker with 0.1 M NaOH solution. 4 g of NaOH pellet was dissolved in 1 L of water. From the previous studies, combination of 8% of MDEA and 4% of AMP gave the highest absorption rate which is 66.8%. The beaker was covered with aluminum foil. Next, the mixture was stirred on a hot plate magnetic stirrer at 30°C at the speed of 700 rpm for 15 minutes.

Prior to emulsification of MDEA/AMP, an organic phase of kerosene and DOPC and SPAN 80 was prepared. DOPC was dissolve in ethanol, where the solubility of DOPC is 25 mg/ml in ethanol. An organic phase was prepared by following the respective formulation shown in Table 1. The mixture was prepared in the same manner as aqueous phase was prepared in this study.

The emulsion was prepared using the high-performance dispenser Ultra Turrax® T25 with 18G mixing shaft. Water-in-oil emulsion was obtained by homogenizing the aqueous and organic phase that has been produced in the previous step. The kerosene solution of DOPC and SPAN80 was mixed first, and this mixture was then emulsified with an aqueous phase. The emulsification process started where organic phase was place on the homogenizer and the homogenizer speed was set at 5000 rpm. Within 2 minutes, aqueous phase was slowly added into the organic phase ready in the beaker. After that, the emulsion was homogenized again at 1000 rpm for another 7 minutes until milky emulsion was formed

Table 1: Formulation and condition used during emulsion preparation for different concentration of cosurfactant.

Sample number	100 mL Organic Phase	100 mL Aqueous Phase
1	92% v/v Kerosene : 8% Span 80	8% v/v MDEA : 88% NaOH : 4% v/v AMP
2		8% v/v MDEA : 92% NaOH
3	92% v/v Kerosene : 8% DOPC	8% v/v MDEA : 88% NaOH : 4% v/v AMP
4	92% v/v Kerosene : 4% v/v DOPC : 4% v/v Span 80	8% v/v MDEA : 88% NaOH : 4% v/v AMP
5		8% v/v MDEA : 92% NaOH

2.3 Stability of Emulsion

Stability test was conducted by water break-up test, where the prepared samples was filled in graduated test tubes and placed in a room at temperature 25°C. After 24 hours, total volume of separated layers was measured. The stability of the emulsion was evaluated by using the equation below. The emulsion is considered stable if the separated layer is less than 10%.

Stability of emulsion (%);

$$= \frac{V_T - V_S}{V_T} X\ 100 \qquad (1)$$

Where V_T = Total volume (mL), V_S = Separated volume (mL)

2.4 Carbon Dioxide Absorption

Rotating disc contactor (RDC) column system was used in the study of CO_2 gas absorption. RDC will increase the contact time between the gas of CO_2 and emulsion. Firstly, in the determination of CO_2 gas absorbed, the pure CO_2 gas was injected into the gas chromatography (GC) to determine the quantity of CO_2 before absorption. The emulsion was then poured into the RDC. The gas flowed into RDC at the flowrate of 20 L/min for 1 minute and CO_2 was allowed to absorb for 10 minutes. The pressure in RDC was 20 kPa and the stirring speed was set at 450-500 rpm. In the RDC, the gas mixture flows upward in the circular motion. The amount of CO_2 gas leaving the RDC was measured by GC. The result was compared with result obtained when the gas mixture was injected into the GC without passing through the emulsion. The result was used to analyze the percentage of CO_2 removal from the injected pure gas of CO_2.

3. RESULTS AND DISCUSSION

In this study, there are several variables that affect and influence the absorption of CO_2 through the emulsion. The emulsion was prepared by different aqueous phase which are MDEA/AMP and MDEA and different organic phase which are SPAN 80, DOPC and DOPC/Span 80. The stability and the viscosity of the emulsion measured. The performance of the emulsion was evaluated based on CO_2 absorption.

The emulsion was prepared by homogenizing aqueous phase and organic phase using homogenizer until milky emulsion was formed. The aqueous phase used was MDEA/AMP and MDEA in NaOH solution and surfactants, Span 80 and DOPC was mixed with kerosene. The emulsion formulation shown in Table 2 was prepared to formed water-in-oil emulsion and to study the absorption of CO_2 through an emulsion.

Table 2: Formulation and condition used during emulsion preparation.

Sample number	100 mL Organic Phase	100 mL Aqueous Phase
1	92% v/v Kerosene : 8% Span 80	8% v/v MDEA : 88% NaOH : 4% v/v AMP
2		8% v/v MDEA : 92% NaOH
3	92% v/v Kerosene : 8% DOPC	8% v/v MDEA : 88% NaOH : 4% v/v AMP
4	92% v/v Kerosene : 4% v/v DOPC : 4% v/v Span 80	8% v/v MDEA : 88% NaOH : 4% v/v AMP
5		8% v/v MDEA : 92% NaOH
Emulsification speed	10,000 rpm	
Emulsification time	5 minutes	
Agitation speed	500 rpm	
Absorption time	10 inutes	

3.1 Stability of Emulsion

The stability of the emulsion was measured after 24 hours from emulsion preparation. The stability of emulsion was evaluated by using equation (1). The result from calculation of the sample was presented in Figure 1 and was discussed in this study.
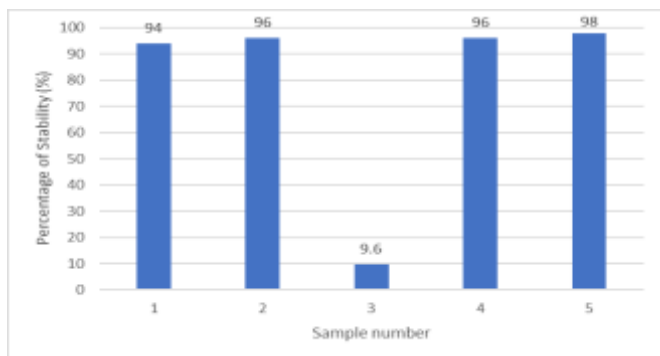

Figure 1: The stability of emulsion using different formulation

Based on Figure 1, Sample 1 shows a reading of 94% in terms of stability when the emulsion contained Span 80 and MDEA/AMP as surfactant and extractant respectively. The formulation is referred to Table 2, the stability of Sample 2 (96%) which is slightly higher than stability of Sample 1 (94%). This is due to the different amine formulation, but both sample used Span 80 as a surfactant.

DOPC was introduced to form an adhesive emulsion due to its ability as phospholipids to form bilayers from two monolayers of each droplet surface. Based on Figure 1, the stability of emulsion was at lowest which at 9.6% when DOPC acted as the only surfactant for sample 3. This finding agreed with paper published by Kim et al., where the researcher reported that DOPC is typically unstable because of its molecular structure whose HLB value is moderate(7), therefore resulting in the poor stability of W/O emulsion [6].

As DOPC was proved to formed unstable emulsion, to form a stable adhesive emulsion, another formulation was prepared by adding Span 80 to DOPC to increase the stability. This is because the molecular shape of Span 80 becomes a complimentary to that of DOPC thus able to stabilize the emulsion [6]. Figure 1 shows that the stability of emulsion for Sample 4 was recorded at 96% using MDEA/AMP as extractant in emulsion formulation. Meanwhile, MDEA as aqueous phase also shows the same patterns as Sample 5 stability of emulsion was measured at 98% compared to Sample 4 at 96%. Thus, this finding proved that by adding DOPC/Span 80 in organic phase, a stable adhesive emulsion was formed.

Figure 2 shows the emulsion physical appearance on stability test after 24 hours of emulsion formation. Based on Figure 2(a) an adhesive emulsion shows a highly stable emulsion after 24 hours. Figure 2(b) clearly shows that the emulsion was separated into 3 layers (oil, emulsion and aqueous) that shows the emulsion undergoes demulsification process [10,11]. A stable emulsion is important in CO_2 absorption process. Figure 2(b) shows the emulsion after 24 hours, when DOPC was used as surfactant. DOPC covered emulsion droplets could not act as stabilizer themselves, the molecular shape need to be complemented with Span 80. Result from Span 80 as cosurfactant for DOPC in DOPC/Span 80 surfactant system giving a physical appearance of emulsion after stability test shown in Figure 2(a).

Figure 2: (a) Sample 5 (DOPC/SPAN 80-surfactant) and (b) Sample 3 (DOPC-surfactant)

3.2 Viscosity of Emulsion

The study of viscosity in this experiment will help further understand the mass transfer process that occur in the absorption. In this study the viscosity of emulsion was measured using Brookfield Viscometer Model DV-I Prime. The viscosity has great influence in providing information for emulsification and stability of emulsion [10]. If the solution is highly viscous, it resulted in stable emulsion, but too high viscosity may reduce the dispersion of droplets in the organic phase [12]. Figure 3 shows the recorded data for viscosity based on different formulation.
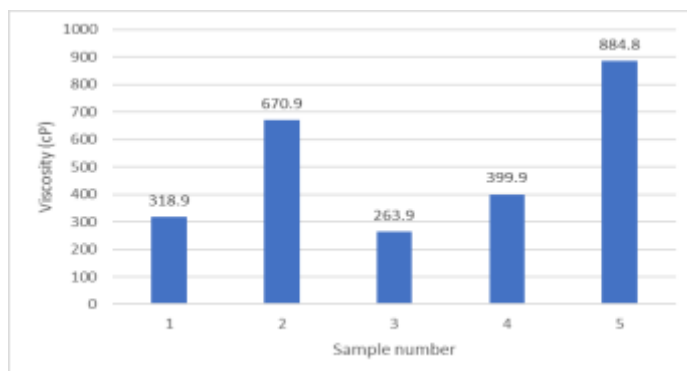

Figure 3: Viscosity of the emulsion based on formulation

Figure 3 shows the viscosity value of Sample 1 (318.9 cP), which is lower than Sample 2 (670.9 cP). Both samples used Span 80 as surfactant but different amine formulation. The viscosity value of sample containing DOPC as surfactant (Sample 3), where it is the lowest (263.9 cP). It shows that as the viscosity of emulsion is lower the stability also decreases. This is due to that DOPC molecular structure, cannot retained the shape of globules, thus poor in stabilized a W/O emulsion. Adding Span 80 as cosurfactant to DOPC resulting in higher viscosity value that shown in Figure 3. Viscosities of Sample 4 and Sample 5 is 399.9 cP and 884.8 cP respectively. This is because, Span 80 contain a relatively small hydrophilic head groups, compared to long hydrophobic carbon chain, thus resulting it's to have low HLB number where it able to stabilize W/O emulsion. In addition, a cone shape molecular geometry possibly induced a better packed interface with phospholipids, preventing coalescence between dispersed droplets in the emulsion [6]. Increasing viscosity is one of methods to increase the stability of emulsion globules [7]. Viscosity of emulsion increase as SPAN 80 used as cosurfactant complementary to DOPC, however increase in viscosity may inhibit the absorption process as it can reduce the solubility of CO_2 [13]. High stability emulsion is necessary to maintain the emulsion formed in the absorption process, but it should allow CO_2 to diffuse through it. The relationship between viscosity and stability was shown in Figure 4.
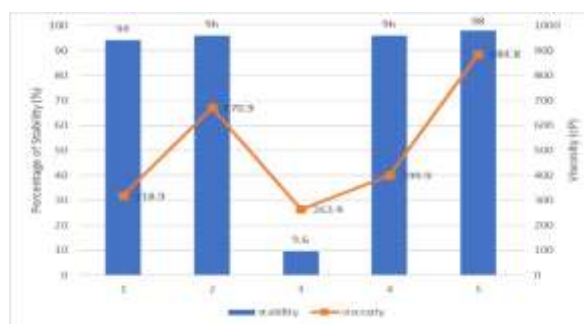

Figure 4: Relationship between viscosity and stability of an emulsion

Figure 4 shows the viscosity of emulsion is proportional to the stability of emulsion. The value in Figure 4 shows a relationship between viscosity and stability which higher value of viscosity the stable emulsion [9]. As reported by Sreedhar et. at., highly viscous may inhibit the absorption produce as it reduces the solubility of CO_2 [13]. A summary from Figure 4, the stable the emulsion indicates the higher number of viscosity value.

3.3 Carbon Dioxide Removal

In this study, the most important aspect is to investigate the percentage of CO_2 when emulsion was applied in the separation process. By introducing adhesive emulsion, the stability increased that resulting a stable medium for absorption of CO_2 gas. In this study, the performance of emulsion was determined by CO_2 gas removal. CO_2 gas was used as feed gas, passing through the RDC column that contained emulsion. The amount of CO_2 gas

absorbed was calculated and the effect of different surfactant on the absorption was analyzed. Figure 5 shows the amount of carbon dioxide absorbed for different emulsion formulation.
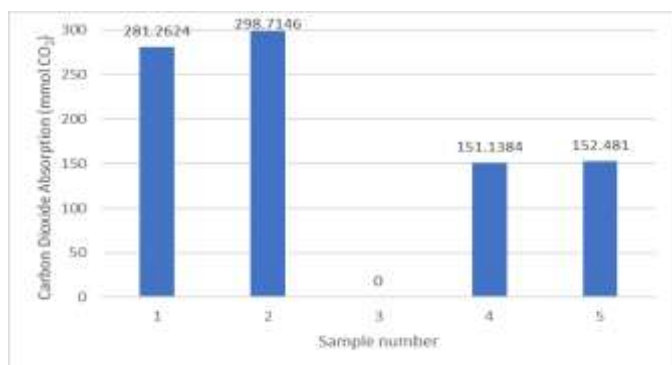

Figure 5: Percentage of CO_2 absorption using different emulsion formulation

Based on Figure 5, using MDEA/AMP as extractant (Sample 1), the emulsion absorbed 281.26 mmol CO_2, while emulsion containing MDEA as extractant (Sample 2) absorbed 296.71 mmol CO_2. This is due to different formulation of aqueous phase used in the emulsion. The absorption of CO_2 using DOPC as surfactant shows no CO_2 removal because demulsification has occurred. DOPC itself cannot retained the emulsion, thus leads to breakdowns of emulsion. Due to this breakdown, the separation process cannot take place as no medium for diffusion of CO_2 to occur in the solution [5]. A cosurfactant that was introduced in this study formed an adhesive emulsion which lead highly stable emulsion. As shown in Figure 5, CO_2 absorption for Sample 4 was only at 151.14 mmol of CO_2 which is slightly lower than Sample 5. (152.48 mmol of CO_2) The differences of absorption capacity are influenced by stability and viscosity of the emulsion.

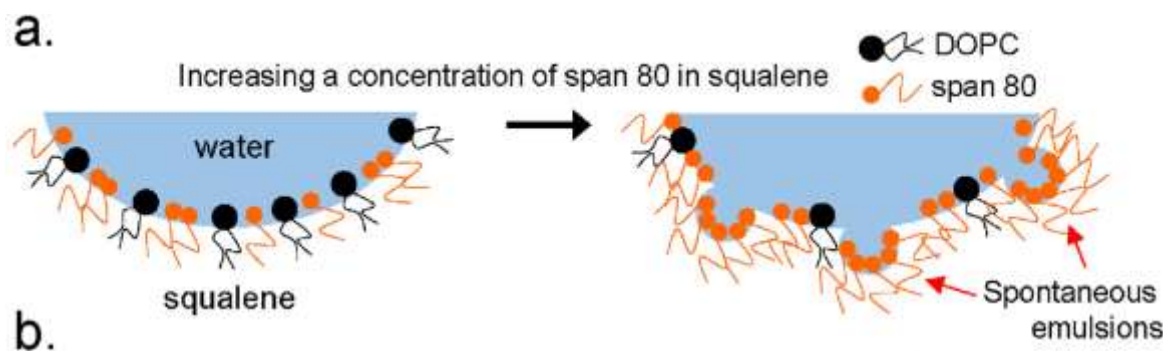CO_2 removal was less in DOPC/Span 80 system as compared to Span 80 as surfactant. This result shows that, even though the emulsion stable, it does not have the ability to increase the absorption of CO_2 gas. Figure 6 shows a correlation between stability and the amount of CO_2 absorbed. The stability is linked with viscosity (Figure 4), where high viscosity, may inhibit the absorption of CO_2 [5]. lower CO_2 absorption may also due to the concentration of surfactant employed. Increase the surfactant concentrations leads to a higher viscosity of the W/O emulsion and does not favor the extraction kinetics [4]. Thus, it may create a resistance for CO_2 to diffuse through the emulsion. It was also reported that surfactant plays an important role during the absorption because excessive stability of emulsion may reduce the efficiency of separation process [4].
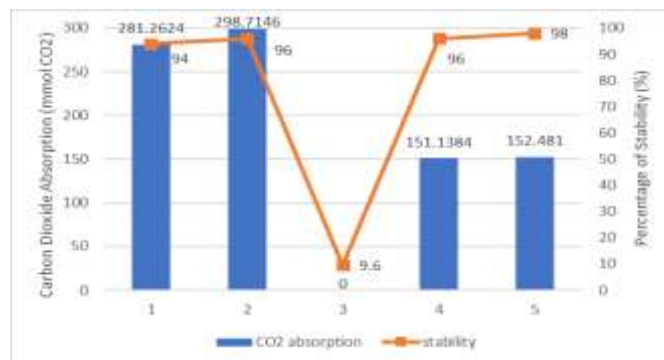

Figure 6: Relationship between amount of CO_2 absorbed and stability of an emulsion

It is also suggested that the use of cosurfactant DOPC/Span 80 has produced a stable emulsion, but it does not facilitate CO_2 absorption due to its molecular structure as shown in Figure 7. As it forms an adhesive emulsion and it also create a resistance for CO_2 to pass through and diffuse through the interface layer.

Figure 7: The structure of emulsion formed as DOPC/Span 80 act as surfactant [6]

Therefore, it is proved that mass transfer of CO_2 in an adhesive emulsion is having high CO_2 resistance. This study shows that the stability of emulsion does not assured high CO_2 absorption. In summary, a selection of surfactant as an emulsifier is vital for diffusion to occur, even if it does produce a great stability of an emulsion but does not provide a good medium for absorption process to occur thus it is not a suitable surfactant to be used in a formulation.

4. CONCLUSION

An experimental research was carried out to study the role of cosurfactant in stabilizing the emulsion in order to achieve a higher efficiency of absorption. The result drawn from this study, provides a better understanding on the relationship between the surfactant and the rate of absorption. The result shows that even the emulsion is stable, it does not facilitate the absorption process. This is due to the molecular structure of the surfactant that surround the emulsion droplet may create a resistance for CO_2 gas to diffuse. The stable the emulsion, the higher the value of viscosity value and thus becomes a resistance for CO_2 to diffuse. In conclusion, it is very vital decision in selecting a suitable surfactant as an emulsifier for CO_2 removal in the absorption process. This study suggesting, by reducing the resistance in the emulsion may increase the rate of absorption to occur in the emulsion thus increasing the efficiency of separating the CO_2 gas through an emulsion.

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