

Emulsion Stability and CO₂ Removal Performance of MDEA-AMP Blends with Tween-80 Surfactants

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ABSTRACT

Carbon dioxide (CO₂) is a corrosive and inflammable gas found in natural gas. The most widely technique used for CO₂ separation in the natural gas industry is via amine absorption method. However, due to the corrosive nature of amines, researchers actively looking for an alternative method to separate CO₂. Therefore, the emulsion liquid membrane (ELM) was developed to address this issue. In spite of that, it still remains as challenge to find suitable formulation to produce stable emulsion with good CO₂ removal performance. In this study, the amine blend emulsion containing Methyl-diethanolamine (MDEA) and 2-amino-2-methyl-1-propanol (AMP) with Tween-80 (Polysorbate-80) were prepared. An aqueous phase was formed by blending of MDEA and AMP in sodium hydroxide (NaOH) solution. The organic phase composed of kerosene and Tween-80 used as surfactant. The effect of varying concentrations of Tween-80 on the emulsion stability and CO₂ absorption capacity of ELM were investigated in this study. The emulsion was prepared by mixing the aqueous and organic phases for 5 minutes at a speed of 10,000 rpm until it become homogenous. The CO₂ absorption capacity was conducted in a rotating disc contactor column with a 2-bar pressure of CO₂ gas supply. This study demonstrated that, by blending of 8% v/v MDEA and 4% v/v AMP with 10% v/v Tween-80, 56.89% of CO₂ removal could be achieved while maintaining an emulsion stability of 95%.

Keywords: Carbon dioxide; emulsion liquid membrane; amine absorption; emulsion stability; Tween-80

INTRODUCTION

The separation of CO₂ from the industrial natural gas stream is an important step in the natural gas sweetening process. Various technology for CO₂ removal had previously been conducted by various researchers. These includes chemical solvent absorption, physical absorption (Kothandaraman et al. 2009; Lang et al. 2017; Wilk et al. 2017), cryogenic separation (Xu et al. 2014; Maqsood et al. 2014), adsorption (Madzaki et al. 2018) and membrane separation (Adewole et al. 2013; Xu et al. 2018).

Furthermore, emulsion liquid membrane (ELM) has been presented as an alternative to conventional amine-based CO₂ separation technologies. Simultaneous purification and concentration of the solute is achievable with a liquid membrane (Dolmat et al. 2014; Suahadah et al. 2015; Najib et al. 2022; Najib et al. 2023).

Emulsion Liquid Membrane (ELM)-based separation methods have proven to be an attractive and efficient method for removing carbon dioxide, hazardous metal ions, organic and inorganic acids and industrial contaminants from variety of aqueous waste effluent streams (Kumar et

al. 2019; Zaulkiflee et al. 2022). The efficiency of emulsion liquid membrane is depending on the emulsion stability, the diffusivity of adsorbate, which is proportional to its surface area and the membrane's thickness. Following Norman Li's 1968 discovery of the ELM methodology, ELM gained prominence among traditional separation methods. However, ELM processes have issues related with emulsion instability, membrane breakdown owing to swelling during high shear rates, and stress rates during the separation process, all of which reduced the overall efficiency of the ELM processes (Al-Ani et al. 2021).

The quality of the formulation depends on the components selected for emulsion liquid membrane. This includes the selection of appropriate surfactant, diluents, stripping agent, and carrier agent for the application in question. ELM is divided into two phases: the organic phase and the aqueous phase. A surfactant with a polar head group and a non-polar tail acts as an emulsifying agent, affecting not only the stability of the emulsion but also other variables such as permeability, water solubility, and mass transfer resistance (Al-Mohammedawi et al. 2022). There are multiple types of surfactants that has been used in industry such as Span-80, ECA 4360 and Tween-80. Among these surfactant, Tween-80 received particular interest due to its low cost, low polarity, low toxicity and high solubilization capacity. Furthermore, Tween-80 has hydrophilic-lipophilic balance (HLB) value of 15, which is within the range of HLB 8–18 for emulsifiers (Kassem et al. 2019). Owing to its high-water solubility and HLB of nearly 15, Tween-80 is well suitable for stabilizing lipid as nanocarriers (Whitehurst 2004). Therefore, in this study, the emulsion stability and CO₂ gas removal performance of amine blending between MDEA and AMP with Tween-80 as a surfactant in emulsion liquid membrane formulation will be investigated. The characteristic that affecting the emulsion stability and CO₂ gas removal will be discussed from a viewpoint to produce stable ELM with high CO₂ removal performance.

METHODOLOGY

SYNTHESIS OF MDEA-AMP EMULSION LIQUID MEMBRANE

In this study, the aqueous phase was prepared by using MDEA, AMP, and NaOH. The 100 mL of aqueous phase was produced by mixing of 8 mL of MDEA (8% v/v) and 4 mL (4% v/v) of AMP in 88 mL of 0.1 M NaOH solution and the mixture was stirred for 15 minutes. On the other hand, for organic phase, kerosene and Tween-80 was used.

The 100 mL of organic phase is produced by dissolving varied concentration of Tween-80 (0-10 mL or 0-10% v/v) in kerosene oil and kept stirred for 15 minutes. The stirring speed of the heating plate are set between 600-800 rpm under room temperature condition for the aqueous and organic phase solutions, respectively.

Next, the ultra-high-performance disperser Ultra Turrax® T25 with an 18G mixing shaft is utilized to prepare the emulsion. ELM was prepared by mixing the aqueous and organic phases for 5 minutes at a speed of 10,000 rpm until it become homogeneous. The beaker is filled with a 100 mL of organic phase mixture. The 100 mL aqueous phase mixture poured slowly into the organic phase beaker to form the emulsion. This procedure was repeated using different concentration of Tween-80 which varied from 0% v/v until 10% v/v in organic phase to determine the effect of Tween-80 concentrations on the emulsion stability and CO₂ absorption capacity.

EMULSION STABILITY

Emulsion stability was recorded within 24 hours of emulsion preparation. The stability test was carried out by placing the sample into graduated test tubes and storing it under room temperature condition. The stability of an emulsion is determined by the formation of the membrane phase and the conditions presented during emulsion preparation. The formation of layer in emulsion was measured and observed. The calculation of the emulsion stability can be calculated by Equation 1 as shown below:

$$\text{Stability (\%)} = (VT - VS) / VT \times 100 \quad (1)$$

where VT is referring to total volume (ml), VS is referring to separated volume (ml).

CARBON DIOXIDE ABSORPTION

In this study, CO₂ absorption has been conducted using Rotating Disc Contactor (RDC), similar to Bhatti et al. (2012). The amount of carbon dioxide (CO₂) absorbed in the prepared emulsion was determined by using gas chromatography (GC) connected to a rotating disc contactor (RDC). The RDC is filled with 200 ml of the synthesized emulsion and the stirrer was set up to 500 rpm. Then, the CO₂ gas mixture flowed into the RDC for one minute. Pressure will be measured inside the RDC. After one minute, the flow of gas mixture halted, and the GC reading was taken. The percentage of CO₂ absorption was calculated based on the amount of CO₂ leaving the column.

RESULTS AND DISCUSSION

STABILITY OF EMULSION

The effect of Tween-80 concentration on the stability of emulsion in the MDEA-AMP mixture was investigated in

this study. The stability of the emulsion was measured after 24 hours. The presence of layers in the test tube indicated sedimentation, whereas the presence of two layers indicated emulsion breakdown, as shown in Figure 1.

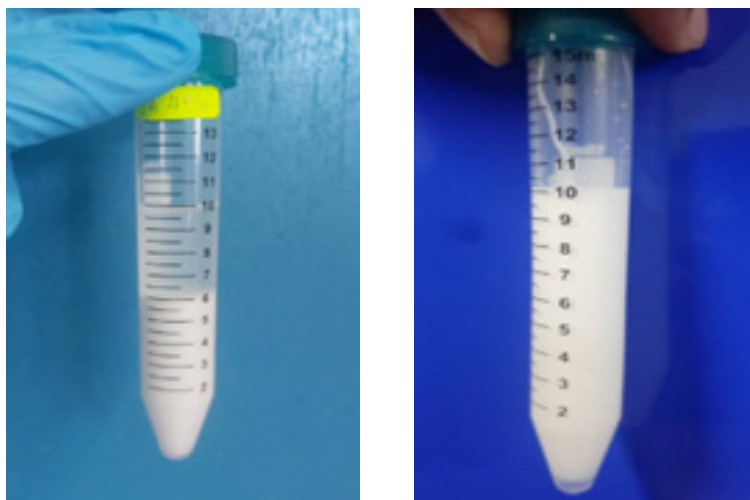


FIGURE 1. Emulsion stability (left) sedimentation and emulsion breakdown (right)

The emulsion stability is strongly influenced by the surfactant concentration. The percentage of emulsion stability as a function of Tween-80 surfactant concentration is shown in Figure 2. The stability of emulsion increases with Tween-80 concentration. The emulsion contains 10%

v/v of Tween-80 exhibited the highest stability of 95%. The proportion of surfactant in the organic phase enhanced the emulsion stability and viscosity, according to Anarakdim et al. (2020). As a result, the emulsion becomes more stable as the Tween-80 concentration increased.

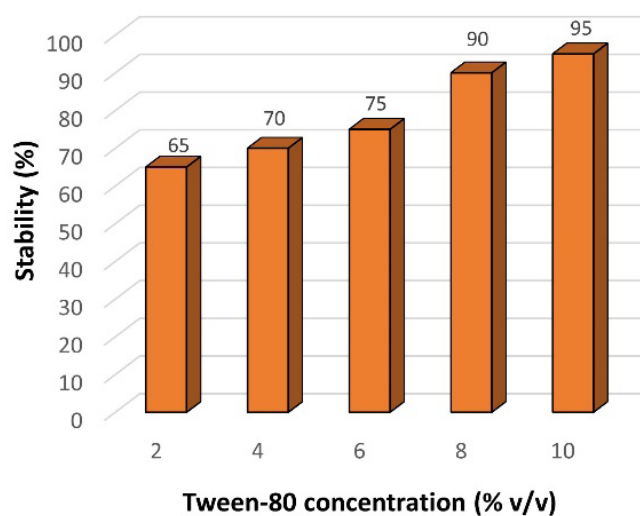


FIGURE 2. The percentage of emulsion stability at different concentration of Tween-80

Emulsions can be stabilized by the absorption of surfactant molecules at the oil-water interface, which

results in a phase boundary with a low free energy. As surfactant solutions are injected into oil alongside the

membrane, the hydrophilic head reacts with the water, while the hydrophobic tail reacts with the emulsion components. In high viscosity diluents such as kerosene, a stable emulsion is formed (Othman et al. 2006). According to Bhatti (2011), emulsion stability resulted in a high CO₂ removal rate because the extractant can react with CO₂ at the gas-liquid interface and diffuse easily. The enhancement of this emulsion system lowers the system's cost and increases the efficiency of CO₂ separation from natural gas.

VISCOSITY OF EMULSION

The viscosity of the emulsion was determined using Programmable Rheometer Brookfield Model DV-III. The viscosity of an emulsion is critical because it provides

information about the degree of emulsification and stability. This is because small particles with a large separation between them take longer to settle down during emulsification. If the solution has a high viscosity, it will form a stable emulsion, since surfactant created more resistance at the interface.

In this study, a membrane phase exhibited high viscosity values, which translated into production of more stable emulsion. As illustrated in Figure 3, as more Tween-80 was added, the viscosity of the emulsion was increased. However, excessive viscosity reduces aqueous dispersion in the organic phase (Othman et al. 2006), which significantly decreases the diffusivity of solute (Skelland and Meng 1999). As a result, the solute diffusivity is decreased, and the extraction rate decreases, posing a problem in the emulsion separation process.

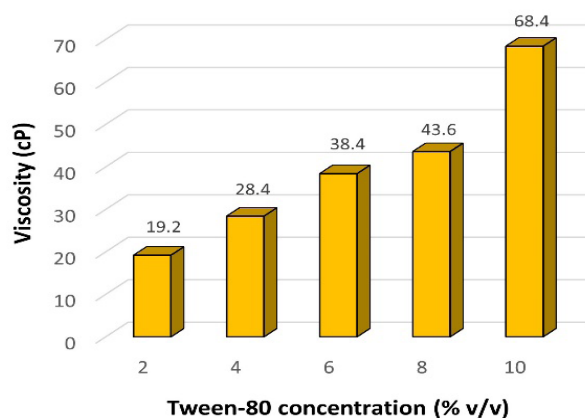


FIGURE 3. The viscosity of emulsion at different concentration of Tween-80

Increasing the concentration of surfactant resulting in the stability of the emulsion. By increasing the surfactant concentration to a certain level, the interfacial tension between the phases decreases, resulting in the formation of finer droplets and a more stable emulsion. However, excess of surfactant may reduce emulsion stability due to the surfactant's tendency for aggregate formation. Both amines and Tween-80 eventually influence the viscosity of the emulsion. Thus, it is critical to select an appropriate amount of amine and surfactant to achieve high CO₂ removal.

RELATIONSHIP BETWEEN EMULSION STABILITY AND VISCOSITY

As observed in Figure 1, only sedimentation occurred in this study, as evidenced by the formation of another layer

on top of the emulsion layer. The viscosity of the emulsion can also be used to determine the sedimentation velocity (Park, 2006). Figure 4 demonstrated that the viscosity of an emulsion is proportional to its stability. As the concentration of Tween-80 increased, the viscosity of the emulsion proportionally increased, resulting in a more stable emulsion, as shown in Figure 4. According to Skelland et al. (1999), increasing the viscosity of a fluid significantly reduces its diffusivity. As a result, this may result in a decrease of solute diffusivity and a decrease in extraction rate. In addition, a higher viscosity emulsion requires more energy to disperse. In this study, high emulsion stability is required together with the capability of removing CO₂ simultaneously.

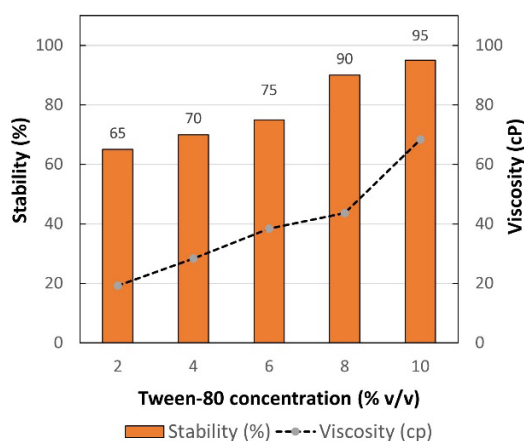


FIGURE 4. Stability and viscosity of emulsion at different concentration of Tween 80

CARBON DIOXIDE REMOVAL PERFORMANCE

In this study, an emulsion liquid membrane containing MDEA and AMP blending were used as a potential alternative method for CO₂ absorption. Blended amine has shown unique and predominant performance while used to capture CO₂ compared with the single amine. The study conducted by Najib (2017) demonstrated that a mixture of MDEA and AMP exhibited higher CO₂ absorption capacity than any primary or secondary amine since CO₂ absorption capacity of AMP is approximately twice than any primary or secondary amine. In addition, AMP which is sterically hindered amine, shows slower CO₂ chemical absorption rate when compared to other primary amine when used as single amine, but exhibited superior CO₂ absorption

capacity when blended with other amines (Magnone et. al 2021).

As discussed earlier, the emulsion becomes more stable as the viscosity of emulsion increases. However, the layer might become thicker and diffusion rate reduced, if the emulsion become too viscous, which may lead to low CO₂ removal (Najib et. al 2023). Thus, it is critical to select an appropriate amount of surfactant to create a stable emulsion with a high CO₂ removal capacity. Figure 5 illustrates the effect of surfactant concentration on the ability to absorb CO₂ under various Tween-80 concentrations. The emulsion containing 10% v/v of Tween-80 exhibited the highest CO₂ removal (56.89 %). As the Tween-80 surfactant concentration increases, the emulsion becomes more stable, allowing for more CO₂ removal.

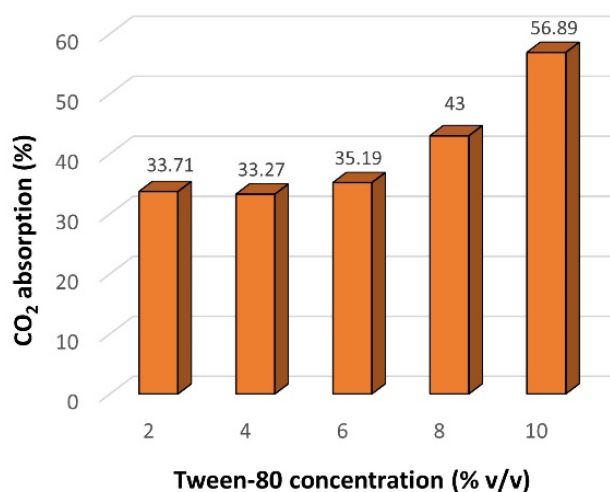


FIGURE 5. The percentage of CO₂ removal under various Tween-80 concentrations

CONCLUSION

This study successfully investigated the effect of Tween-80 surfactant concentrations on emulsion stability, as well as its CO₂ removal performance. The stability of the synthesized emulsion remains high, up to 95%, with minimal emulsion breakup and only sedimentation occurred. Furthermore, the highest CO₂ absorption rate measured in this study was 56.89 % (4% v/v AMP, 8% v/v MDEA and 10% v/v Tween-80).

This study demonstrated that the development of stable amine-blend emulsion liquid membrane with high CO₂ removal capacity can be achieved via blending of MDEA-AMP with appropriate Tween-80 surfactant amount.

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DECLARATION OF COMPETING INTEREST

None

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