Water-in-oil-in-water (W/O/W) emulsion instability in emulsion liquid membrane: membrane breakage

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Abstract. Water-in-oil-in-water (W/O/W) emulsion system in Emulsion liquid Membrane (ELM) consist of three main phases which are membrane phase, internal phase and external phase. However, ELM performance is reported to be heavily affected by the emulsion stability. Instability of emulsions occurred as a result of metastable colloids that are made of two immiscible liquids, where one being dispersed in the other with the presence of surface-active agent. Membrane breakage was identified as one of the causes of emulsion instability. This research work focuses on identifying best condition that records minimal breakage hence, high efficiency of solute removal can be anticipated. Influence of homogenization time and speed, carrier concentration and surfactant concentration on membrane breakage were investigated. Data recorded shows that the emulsion needs to be homogenized at 8000 rpm for 15 mins to obtain minimal breakage of membrane. On top of that, membrane phase consist of 4 wt% of carrier (D2EHPA) and 4 wt% of surfactant (Span 80) dissolved in kerosene is needed. 0.14% of breakage was recorded at the conditions mentioned.

1. Introduction
Emulsion liquid membrane (ELM) is a liquid membrane based on process initially proposed by Li [1] where a primary emulsion is dispersed in the feed phase to be treated. It is a highly effective method for the recovery of different compound contained in wastewater. Basically, ELM comprises of three phases as shown in figure 1, consisting of membrane, internal and external phase [2]. The membrane phase consists of surfactant, diluent and carrier. It is reported that the emulsion requires the presence of surfactant to ensure the stability of the emulsion by reducing the interfacial tension between phases [3]. On the other hand, the existence of carrier in the membrane phase is typically claimed to affect the stability of the emulsion as well. The external phase is the water phase that carries the metal or other elements of interest while the internal phase is another liquid phase that traps the recovered solutes. Both phases are separated by the membrane phase layer.
Basically, ELM is prepared via three main steps. Firstly, the membrane phase and internal phase was prepared prior to emulsification. The emulsification process produces the primary water-in-oil (W/O) emulsion. This process was followed by the dispersion of the primary emulsion in the external phase which forms the water-in-oil-in-water (W/O/W) emulsion system. Solutes will be extracted due to the presence of carrier in ELM. This technique is commonly used for element of metal ions extraction and organics recovery. The process is said to obey the Type II Facilitated Transportation of solute. ELM was reported to successfully remove many types of heavy metals in short time using D2EHPA and Span 80 as carrier and surfactant, respectively. This method was proven to be effective based on report on the extraction of Cr (II) by Acosta et al. [4] while Kusumastuti et al. [5] reported on Cd(II) ions removal. This is because ELM offers fast process of the extraction and allows single phase operation of a stripping extraction process at high surface area to volume ratio.

Achieving maximum solute removal efficiency has always been the target for any liquid membrane system. However, emulsion stability problem in ELM is still continuously discussed by many researchers as it is the most threatening concern for this system. Stability of the emulsion globules is literally known as one of the most serious problems in the application of the ELM for the separation of industrial waste [6] as ELM is thermodynamically unstable it is expected to break once the emulsion is dispersed [7]. Emulsion swelling, membrane breakage and coalescence were reported to cause membrane instability. The membrane breakage is a condition of membrane layer rupture hence, leading to loss of internal phase into the external. This phenomenon has heavily affected the efficiency of the system. The current study focuses on obtaining minimal breakage in ELM via the change of pH of external solution thus tracking of volume change of the external phase can be made.

The current study aims to investigate membrane breakage in ELM which is intended to be used to remove Cu(II) ions from aqueous external phase. The effect of homogenization speed and time as well carrier and surfactant concentration will be looked at to conclude the best condition in achieving minimal membrane breakage in the W/O/W emulsion system.

2. Experimental

2.1. Chemicals

Chemicals used are bis(2-ethylhexyl) phosphate or known as D2EHPA (Sigma Aldrich), Span 80 (Merck), commercial grade kerosene, Copper (II) nitrate (Merck) and hydrochloric acid (Merck). On top of that, the pH of external phase was adjusted by using sodium hydroxide, acetic acid and sodium acetate anhydrous, all supplied by Merck. The function of each chemicals utilized in the experimental works are tabulated in table 1. Solutions were made by using distilled water.
Table 1. Chemicals used and their role

| Phases         | Chemicals                                      |
|----------------|-----------------------------------------------|
| Membrane phase |                                              |
| Diluent        | Kerosene                                      |
| Surfactant     | Span 80                                       |
| Carrier        | D2EHPA                                        |
| Internal phase | Hydrochloric acid (HCl) at 1.0M               |
| External phase | Copper (II) nitrate dissolved in Acetate Buffer |
|                | (pH adjusted to 4)                            |

2.2. Emulsion liquid membrane preparation

All phases in emulsion liquid membrane (ELM) were prepared separately in this study. Firstly, the membrane phase was made by dissolving D2EHPA at concentration ranging from 0 to 8 wt% and Span 80 at concentration ranging from 0 to 5 wt% in kerosene. The membrane phase was then stirred at 300 rpm for 5 mins. 1.0 M of HCl was used as the internal phase in this study. Emulsification process was conducted using homogenizer (WITEG HG-15D) at various speed (5000 rpm, 8000 rpm, 10000 rpm and 15000 rpm). The duration of the process was also varied from 5 to 20 mins. The product of this process is the primary water-in-oil (W/O) emulsion. The emulsion was formed by using membrane to internal phase ratio of 1:3 by volume.

The process was then continued by dispersing the primary W/O emulsion in the external phase that contains 50 ppm of copper (II) nitrate. The external phase solution was made by using acetate buffer solution where the pH was adjusted to 4. Mixing process of these phases resulted in the formation of W/O/W emulsion. The emulsion was then stirred at 300 rpm for 15 mins. Once ended, the content of the vessel was left to settle before the external phase was taken out to measure its final pH.

2.3. Stability analysis

Data of external phase pH is useful to calculate the percentage of membrane breakage. Changes of pH of the external phase signifies the leakage of internal phase into the external. Equation (1) shows the volume of internal phase that has leaked due to breakage of membrane.

\[
V_S = V_{Ext} \cdot \frac{10^{-pH_i} - 10^{-pH}}{10^{-pH} - C_{H^+}^i} 
\]

Where \( V_{Ext} \) denotes the initial volume of the external phase, \( C_{H^+}^i \) is the initial concentration of H\(^+\) in the internal phase while \( pH_i \) and \( pH \) is the pH of external phase before and after extraction of Cu(II) ions, respectively. The pH of the solution was measured using Fisher Scientific accumet AB15 pH meter. Calculated leaked volume of internal phase was later converted into percentage ratio of leaked volume to initial volume of internal phase. Such as, with a ratio of 1:3 (by volume), the system consists of 10 mL of internal phase and 30 mL of membrane phase. Percentage of internal phase leaked into the external can be calculated as:

\[
\text{Breakage (\%)} = \frac{V_S}{V_{Ext}} \times 100
\]
3. Results and discussion

3.1. Effect of homogenization time and speed

The effect of homogenization time and speed on membrane breakage in ELM is presented in figure 2. The study was carried out at homogenization speed of 5000 rpm, 8000 rpm, 10000 rpm and 15000 rpm for 5 to 20 mins. The concentration of carrier and surfactant were kept constant at 4 wt% and 5 wt%, respectively. Sufficient time and appropriate speed of homogenization are crucial factors to entrap the internal phase into the membrane and this parameter was reported to dictate the size of emulsion globules. Data obtained in figure 2 reveals that short emulsification time is unable to produce stable emulsion though the speed of the homogenizer increases. Theoretically, smaller droplets of emulsions are produced as high amount of energy is supplied during emulsification process [8]. This situation later produces sufficiently small emulsion droplets which stabilizes the emulsion. On contrary, longer homogenization time reduces the membrane breakage. Long homogenization time resulted in smaller emulsion droplet size. However, many reported on its counterproductive effect at certain limit where internal phase droplets coalesce and larger droplets were formed [9]. Data reported in figure 2 is in line with this claim. Based on figure 2, it is suggested that 15 mins is the limit before the emulsion showing membrane breakage increment.

On the other hand, the effect of homogenization speed on the occurrence of membrane breakage is apparent. It is presented in figure 2 that the membrane breakage decreases significantly as the speed increases from 5000 rpm to 10000 rpm. The least stable emulsion was produced at low speed (5000 rpm) though time was prolonged where it recorded as high as 15.98% of membrane breakage. However, using two extremes of conditions in this study (high speed and long emulsification time) to homogenize the emulsion does not benefit the system either. As can be seen in the figure, long emulsification time (>10 mins) using 15000 rpm of speed did not minimize the breakage of emulsion. High internal shearing which leads to very high number of internal phase droplets [10] is one of the reason. This condition eases the diffusion of the internal phase into the external. At 15 mins of emulsification, identical percentage of membrane breakage was recorded for both speeds; 8000 rpm and 10000 rpm. Evidently, 8000 rpm shall be selected as the best speed to homogenize the phases for 15 mins. At this condition, only 0.14% of breakage was recorded.

![Figure 2](image-url)  
**Figure 2.** Effect of homogenization speed and time on membrane breakage
3.2. Effect of carrier concentration

Experimental works were performed by using various carrier (D2EHPA) concentrations, from 0 wt% to 7 wt% in the organic membrane phase to elucidate its influence on membrane breakage. The experiments were carried out at homogenization speed of 8000 rpm for 15 mins. It was observed that the carrier concentration also plays a key role in the emulsion stability. Data recorded is as shown in figure 3.

![Figure 3](image)

**Figure 3.** Effect of carrier concentration on membrane breakage (%)

From the figure, it can be concluded that increasing the amount of carrier has improved the stability until 4 wt%. Beyond that, the membrane breakage has shown significant increment. It is claimed that high carrier concentration causes osmotic swelling which promotes breakage [11]. Increasing the concentration of carrier has two main effects. Firstly, it was reported to cause competitive adsorption with surfactant molecules [12]. In this context, surfactant is said to be unable to reduce the interfacial tension, thus reducing emulsion’s stability. Large size of emulsion droplets were produced at this condition and tend coalesce easily. Besides, high concentration of carrier affects the total viscosity of the emulsion. As reported, a viscous emulsion is highly resistance towards shear that may induce membrane breakage. Though it is well known that the rate of facilitated transport of the solute is directly affected by the amount of carrier that is present in the liquid membrane, but sufficient amount of carrier must be identified to avoid the efficiency to be nullified as the emulsion becomes unstable. Based on the data obtained, the best carrier concentration was found to be about 4 wt%.

3.3. Effect of surfactant concentration

The influence of surfactant concentration on the emulsion stability was investigated. In this study, the concentration of the surfactant was varied from 0 wt% to 5 wt% while the carrier concentration was kept constant at 4 wt%. Data collected is presented in figure 4. It was observed that the emulsion stability improves by increasing the surfactant concentration until 4 wt% before showing relatively constant results at 5 wt%. Basically, the presence of surfactant in membrane phase reduces the interfacial tension that exist between the water and oil phases. Even though the presence of surfactant is proven crucial, but its concentration must be ideal to avoid thick surfactant film at the membrane wall. This condition will later increases the mass transfer resistance for the solute to be transported through the membrane layer.

Improved emulsion stability at sufficiently high surfactant concentration (> 4 wt%) is due to the strongly absorbed interfacial film of surfactant [13]. In fact, high concentration of Span 80 alters the total viscosity of emulsion. As discussed in the previous section, viscosity of emulsion played an
important role in determining the stability of an emulsion [10]. In the case of higher surfactant concentration, emulsion stability might be disrupted as critical micelle concentration is reached thus, forming reverse micelle. 4 wt% of Span 80 suffice to be incorporated in membrane phase to form the emulsion.

Figure 4. Effect of surfactant concentration on membrane breakage

4. Conclusion

Emulsion stability in emulsion liquid membrane (ELM) is an unavoidable issue. This study looked at parameters that are important in determining the breakage of the membrane layer. Emulsion homogenized at speed of 8000 rpm for 15 mins showed minimal breakage (0.14%). Varying speed and time were found to heavily influence the stability of the emulsion as the size of the emulsion droplets is dependent on these parameters. To achieve the minimal breakage, as much as 4 wt% of carrier (D2EHPA) and 4 wt% of surfactant (Span 80) are needed.

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