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STABILITY ANALYSIS OF WATER IN OIL EMULSION IN LIQUID MEMBRANE PROCESS

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ABSTRACT

Emulsion liquid membrane (ELM) is one of promising technique in separation process. This process consists of three phases: an external phase, a membrane phase and an internal phase. The membrane phase physically separates the external and internal phases and contains a surfactant to maintain emulsion stability. In this project, the study has highlighted the importance of emulsion stability in emulsion liquid membrane process. The emulsion liquid membrane consist of Cyanex 302 as a carrier, kerosene as organic solvent, Span 80 as an emulsifying agent and sulphuric acid as stripping agent. The important factors studied which affect the ELM stability are emulsification time (4–20 min), agitation speed (200–400 rpm); the concentrations of surfactant (1–9 % w/v) and carrier (0.1 -0.9 M). The results showed that 3% w/v Span 80, 0.1 M Cyanex 302, 5 minute emulsification time and 350 rpm agitation speed is sufficient to form stable emulsion.

Key Words : Emulsion, Liquid membrane, Stability, Span 80, Cyanex 302.

1.0 INTRODUCTION

Emulsion liquid membrane (ELM) separation technique, invented by Li [1] has been regarded as an emerging separation technology and extensively examined for potential applications in such fields as hydrometallurgy, environmental engineering, biochemical engineering, pharmaceutical engineering and food industry. Emulsion liquid membranes (ELM) consist of an aqueous phase (internal receptor phase) stabilized by oil soluble surfactants and dispersed as very fine droplets (1–10 mm) inside an oil phase (membrane phase). The resulting liquid membrane, or water-in-oil emulsion, is further dispersed as emulsion globules (0.1–2mm) in another aqueous solution (external donor phase). This multiple emulsion consists of small droplets that have in turn smaller droplets inside them. The immiscible phase separates the internal droplets from the continuous external phase act as liquid membrane. For this reason, multiple emulsions are also known as liquid surfactant membrane [2].

There are two types of multiple emulsion such as water/oil/water (W/O/W) or oil/water/oil (O/W/O). The most common multiple emulsion is of the water/oil/water (W/O/W). Multiple emulsions have been extensively studied due to their potential application in separation process. Their instability has been for long time problem in industrial and pharmaceutical applications. Therefore, the multiple emulsions have to be stable enough to permit separation process. But, it has to be sufficiently unstable to coalescence the emulsion and break the membrane so as to recover the separated

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components; a compromise must be kept between two antagonistic characteristic, which has to be stable and unstable at the same time. The instability of the multiple emulsions has to be controlled so that the component to be released is stable enough to permit the release by diffusion through the membrane.

Two mechanism are important which the transfer of the component through the liquid membrane and the breaking of the droplets at the proper time. Of course, the two mechanisms occur simultaneously in multiple emulsions. The mechanism of swelling of the emulsion droplets until their broke up occurs when the internal droplets have more concentrated solution than the continuous external phase. This creates an osmotic pressure difference, which make the water diffuse from external phase to internal phase, thus the droplets grow and can eventually break. When this happens, the rheological properties change due to the change in dispersed phase ratio [3].

The present study will examine the stability of water in oil emulsion at various condition and formulation. The study also examine the stability of water in oil in water emulsion during the extraction process.

2.0 EXPERIMENTAL

2.1 Materials and Solution

In this study, a model system has used to permit accurate investigation of the parameter understudied. It consists of organic phase, internal phase and external pure water. Liquid membranes consist of three main components such as carrier, diluents, and surfactant. The membrane phase used is a homogeneous mixture of kerosene as organic solvent, SPAN-80 as the surfactant and Cyanex 302 as the carrier. Kerosene was obtained from Fluka Chemika, Sulphuric acid from quality reagent chemical. The internal stripping phase is an aqueous solution of sulphuric acid. The external phase used is pure water.

2.2 Preparation of W/O and W/O/W

In 50 ml beaker, 5 ml of kerosene, carrier (0.1 -0.9 molar) and span 80 [2–12% w/v] in organic solvent (kerosene) are emulsified at stirring speed (5000 rpm) by homogenizer. 5 ml of H_2SO_4 is drop wise to the stirred organic phase until 1:1 volume ratio of organic membrane solution to stripping solution. The solution is stirred continuously to obtain a white water in oil emulsion.

In 50 ml beaker, 10 ml of the prepared ELM (organic phase and internal phase) is added to 25 ml of external aqueous solution (pure water in the case of measuring the emulsion stability or emulsion breakage). The contents are stirred by means of jar tester stirrers at speeds (200-350 rpm) for a 5 minute. The double emulsion (W/O/W) is allowed to be spontaneously separated in separating funnel and the feed phase (external aqueous phase) is filtered.

2.3 Emulsion stability measurement

Leakage and membrane breakage measurement

Measuring the breaking rate of the emulsion carried out by contacting the emulsion with an external phase of pure water. The double emulsion (W/O/W) is allowed to be

spontaneously separated in separating funnel and the feed phase (external aqueous phase) is filtered. The volume of the emulsion recorded after transferred to the graduated cylinder.

Water break up measurement

Water breaks-up test is the most and commonly used test for the stability of emulsion. The principle of this test is to visually observe the rate and amount of free water separated from the emulsion system. The freshly prepared emulsion is transferred to a graduated cylinder of suitable size according to the amount of sample used. The amount of free water separated from the emulsion is observed until the emulsion break and formed water.

3.0 RESULTS AND DISCUSSION

3.1 Stability of Water in Oil in Water (W/O/W) System

Effect of surfactant concentration

Surfactant concentration is one of the most important factors influencing the stability of emulsions. Span 80 was used as surfactant because the HLB value is 4.3 which can favors W/O emulsion. The Span 80 being lipohilic, stabilizes water in oil emulsions following Bancroft's rule, which states that the dispersed is one where the surfactant has higher affinity. It is observed that the increase in concentration of surfactant increases stability and any further increase in surfactant concentration increase the membrane breakage. This is because an increase in surfactant concentration causes Oswald ripening and breakage, which in turn leads to increase in swelling and leakage. The effect of surfactant concentration on the behavior of the emulsion stability is presented in Figure 1.

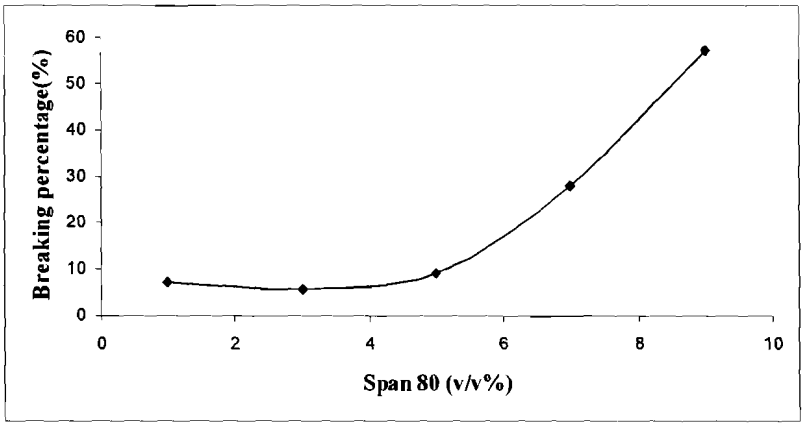

Figure 1 Relationship between breaking (%) and Span 80 concentration (Experimental Conditions: Oil phase= kerosene, water phase: 0.5M sulphuric acid, emulsifications speed: 5000 rpm, Cyanex 302 = 0.1 M, emulsification time: 5 minutes, temperature: 27°C)

Effect of emulsification time

The size of the globules strongly depends on the emulsification time and agitation speed. The emulsion globules are typically in the range of 0.05 to 0.2 cm in diameter [4]. A very large number of emulsion globules can be formed easily to produce a very large mass transfer area adjacent to the external feed phase. As shown from the Figure 2, breaking percentage higher for insufficient emulsification time (<5 min) because the droplets have a large size, which leads to their coalescence. As mixing time proceeds, the breakage rate decreases. It is remarkable that when these drops become smaller they will take much more time to coalesce as reported by Bourenane et al.[5].

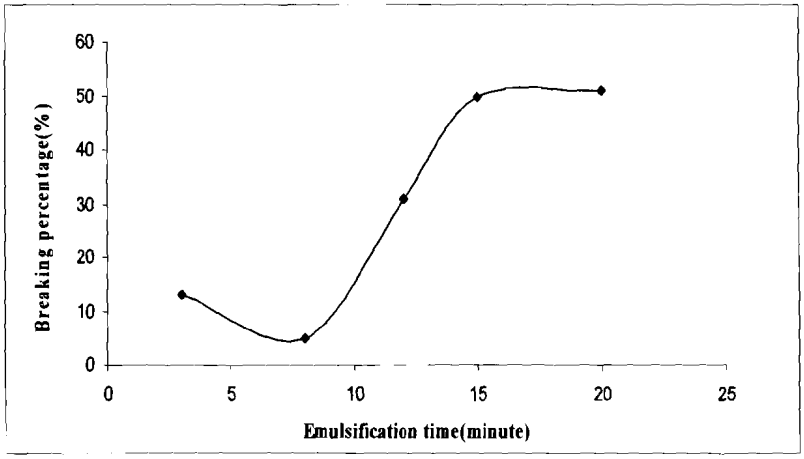

Figure 2 Relationship between breaking (%) and emulsification time (Experimental Conditions: Oil phase= kerosene, water phase: 0.5 M sulphuric acid, emulsifications speed: 5000 rpm, Span 80 = 2 %w/v, Cyanex 302 = 0.1 M, mixing speed = 350 rpm, temperature: 27°C).

It was observed that increases in emulsification time it will decrease the emulsion stability. Membrane breakage was increased after 8 minutes emulsification times. The longer mixing time caused transfer water inside the internal phase. It caused the membrane to swell and might have breakage of the emulsion. Besides, the effectiveness of emulsifier will be decreased because the intense stirring will cause the emulsifier to drop out from the oil-water interface. An increase in mixing time causes high shear due to which the emulsion breaks.

Effect of stirring speed

In order to create a large interfacial area for mass transfer, a relatively high stirring speed is required. Usually, increasing the stirring speed could increase the mass transfer rate, but it will also increase the shear energy, thus increasing the membrane breakage. Figure 3 shows the effects of stirring speeds on the membrane breakage.

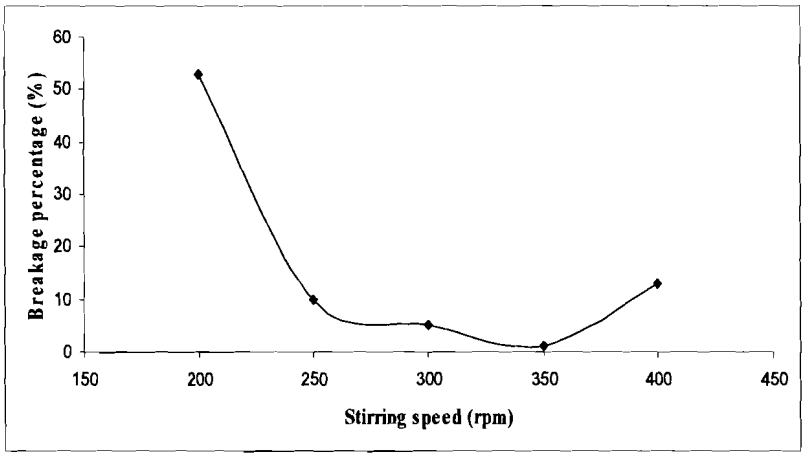

Figure 3 Relationship between breaking (%) and Mixing speed (ExperimentalConditions: Oil phase= kerosene, water phase: 0.5M sulphuric acid, Span 80 = 2 % w/v, Cyanex 302 = 0.1 M, emulsifications speed: 5000 rpm, emulsification time: 5 minutes, temperature: 27°C).

The results showed the following pattern: at the slowest speed, the breaking is the higher and as the speed is increased, the breaking of the emulsions least until a limit tends to be reached. It is evident from the figure that stirring at 350 rpm gives a lower breakage percentage. And there exists a "critical stirring speed" above 350 rpm which membrane breakage increases dramatically. Stirring speed is also an important factor affecting emulsion swelling. Therefore, it is very important to select a suitable stirring speed and keep stable mixing conditions during the process in order to maintain adequate membrane stability and minimize the emulsion swelling.

Effect of carrier concentration

Carrier concentration plays an important role in emulsion liquid membrane formulation. Increasing the amount of carrier led to a decrease in the stability of the emulsion. This behavior is due to the interfacial properties of the Cyanex 302 that forms a reversed emulsion O/W, which leads to the rupture of the emulsion. A very high content of carrier in the membrane does not result in a benefit due to the increase in viscosity, which leads to larger globules. Figure 4 shows the effect of Cyanex concentration on the emulsion breakage.

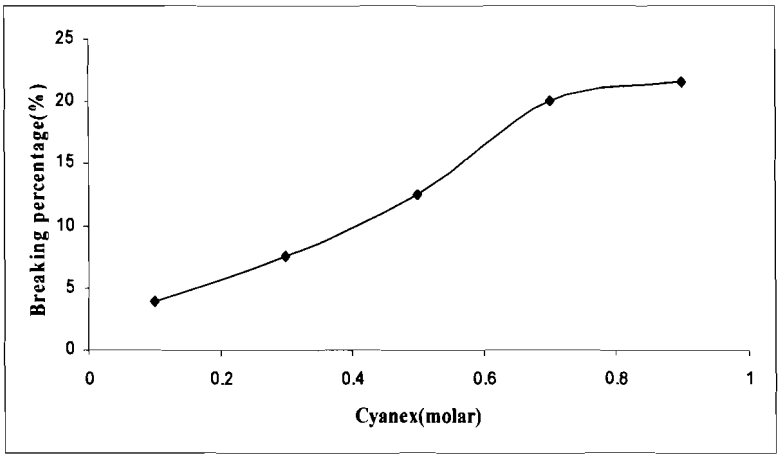

Figure 4: Relationship between breaking (%) and Cyanex 302 concentration (Experimental Conditions: Oil phase= kerosene, water phase: 0.5 M sulphuric acid, emulsifications speed: 5000 rpm, emulsification time: 5 minutes, mixing speed= 350 rpm, temperature: 27°C).

Another reason is with increase in carrier concentration, swelling of the emulsion was also increased which dilutes the aqueous receiving phase and decreases the efficiency of the process. This result coincides with the observations by Draxler and Marr [6, 7] and Hirato et al.[8]. High concentrations in the membrane phase have been observed to lead to high osmotic swelling and high rates of membrane breakdown.

3.2 Stability of Water in oil (W/O) Emulsion

The selection of the liquid membrane components in the emulsion liquid membrane system is important for stability. The factors such as the surfactant concentration and the internal droplet size distribution are crucial to membrane stability for perfect separation efficiency of emulsion liquid membrane systems.

Effect of surfactant concentration

The result shows that the stability increased with increasing surfactant concentration. From the Table 1, 3% (w/v) Span 80 is enough to form stable emulsion, increasing its concentration from 5% to 7% does not make any large difference in water separation. Primary driving force for the phase separation is droplet interfacial free energy [9]. Surfactant concentrates at the oil-water interface and it increase the stability by lowering interfacial tension. In addition, reduction in interfacial tension facilitates emulsion formation and prevents immediate droplet re-coalescence during preparation. However, for obtaining long term emulsion stability, the strength of the interfacial film formed by a surfactant has been reported to be more important than its effect on interfacial tension [9, 10].

Table 1 Effect of surfactant concentration on emulsion stability

Day	Span 80			
	1w/v%	3 w/v%	5 w/v%	7 w/v%
1-12	0	0	0	0
13	0	0	0	0
14	0.5	0	0	0
15	-	0	0	0
16	-	0	0	0
17	-	0	0	0
18	-	0.4	0	0
19	-	-	0	0
20	-	-	0.5	0
21	-	-	-	0
22	-	-	-	0.3

Effect of emulsification time

Emulsification time also play important role in making emulsion liquid membrane. The stability of emulsion is always affected adversely by the shear exerted during agitation (Thien et al., 1990). If the time of agitation too long, the shear exerted on W/O emulsion particle may break the membrane. Besides, the effectiveness of emulsifier will be decreased because the intense stirring will cause the emulsifier to drop out from the oil-water interface. Hence, the stability decreased with less emulsifier content in emulsion. Tables 4.2 show the stability of emulsion when using different emulsification time.

Table 2 Effect of emulsification time on emulsion stability

Day	Time (minute)			
	5	10	15	20
1-16	0	0	0	0
17	0	0	0	0
18	0	0	0	0.5
19	0	0	0.4	-
20	0	0	-	-
21	0	0.5	-	-
22	0	-	-	-
23	0	-	-	-
24	0.5	-	-	-

Effect of Homogenizer Speed

Emulsification is usually achieved by the application of mechanical energy. The agitation intensity is believed to have great influence on the droplet size of the dispersed phase, higher agitation intensity is reported to produce smaller droplet size with greater interfacial area, thus stabilized the emulsion. During emulsification process the

interfacial area between two liquid increases. Liquid tends to minimize this surface area; therefore mechanical energy is required for emulsification proceed. Table 4.3 shows the stability test for various homogenizer speeds. A stirring speed very higher, however not required because higher stirring speed will lead the emulsifier to break away from the oil-ware interface.

Table 3 Effect of homogenizer speed on emulsion stability

Day	Homogenizer Speed (rpm)			
	5000	**6000**	**7000**	**8000**
1-9	0	0	0	0
10	0	0	0	0
11	0.3	0	0	0
12	-	0	0	0
13	-	0.4	0.4	0
14	-	-	-	0
15	-	-	-	0.3

4.0 CONCLUSION

The influence of the stirring speed (200–450) rpm, emulsification time (3–20) minutes, surfactant concentration (1–9) % w/v and carrier concentration (0.1-0.9) molar on the stability of the prepared ELM was investigated. The optimum conditions for preparation of stable emulsion were 350 rpm stirring speed, 5 min emulsification time, surfactant concentration 3% w/v and carrier concentration 0.1 molar.

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