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Double Emulsion (Water-in-Oil-in-Water) System in Succinic Acid Extraction - A Stability Study

Norela Jusoh[a,b], Norul Fatiha Mohamed Noah[a,b], Norasikin Othman[a,b,*]

[a]Centre of Lipids Engineering and Applied Research (CLEAR), Ibnu Sina Institute for Scientific and Industrial Research, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor
[b]Department of Chemical Engineering, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor
norasikin@cheme.utm.my

Emulsion liquid membrane (ELM) process is a very promising method for the industrial separation process. This system offers many advantages, including simple operation, high selectivity, low energy requirement, and simultaneous step of extraction and stripping process. One of the most important aspects for a successful ELM process is emulsion stability, which is governed by emulsion swelling and breakage. Research on the stability of ELM system have been widely reported, especially for primary emulsion (water-in-oil) but very limited in double emulsion (water-in-oil-in-water) stability aspect. In this study, the stability of water-in-oil-in-water (W/O/W) was investigated by varying surfactant concentration of sorbitan monooleate (Span 80) and polyoxyethylene sorbitan monooleate (Tween 80), agitation speed, and agitation time. The results showed that the most stable W/O/W emulsion was obtained at 5 % (w/v) Span 80, 1 % (w/v) Tween 80, 300 rpm agitation speed, and 3 min of agitation time with no emulsion breakage or swelling occurred. This stable emulsion system can promote high extraction efficiency, which is 70 % of succinic acid was extracted.

1. Introduction

Emulsion liquid membrane (ELM) is a separation process in which selective transport of one or more solutes can be achieved through a very thin membrane layer between external and internal phase. The ELM system is in the form of double emulsion, normally primary water-in-oil (W/O) emulsion is dispersed in an external aqueous phase, resulting in water-in-oil-in-water (W/O/W) system. ELM provides several advantages such as low energy consumption, fast extraction and high efficiency, potential for removing various solutes at a very low concentration level (Othman et al., 2006), high selectivity (Noah and Othman, 2017), and ease of regeneration of the spent liquid membrane (Li and Calo, 1992). With these advantages, the ELM process becomes an alternative and a promising technology to be applied in research and industry. It was widely studied for industrial separations such as in removing various types of metal ions, organic compounds, and inorganic compounds (Othman et al., 2013).

Recent development in the ELM process of organic compound is in downstream process of bio-succinic acid separation. This is due to the increasing demand of succinic acid as a building block chemical such as poly (1,3-propylene succinate), 1,4-butanediol, n-methyl pyrrolidinone, γ-butyrolactone, and tetrahydrofuran (Lee and Hyun, 2010).

The industrial applications of the ELM process still have been limited due to the instability of the emulsion globules. The prepared emulsion should be sufficiently stable during the dispersion for solute extraction. Unstable emulsion resulted in emulsion breakage or swelling. Emulsion breakage can cause release of the internal stripping solution to the feed phase and will reduce the extraction performance (Ho and Kamalesh, 1992). Emulsion swelling resulting in destructive effect to the system because it can reduce membrane thickness, diluting the recovered solute, and decreasing the driving force for the extraction (Park et al., 2004). Too stable emulsion may result in difficulties during demulsification for solute recovery and liquid membrane regeneration. Sulaiman et al. (2013) carried out a study to investigate the emulsion liquid membrane stability. It was found that the emulsion stability was influenced by the emulsion formulation and condition of

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emulsification. An appropriate condition also crucial to maintain the emulsion stability during the extraction process.

Studies on the primary emulsion stability was widely reported, but very limited on the double emulsion stability. In this study, the investigation of the effect of Span 80 and Tween 80 concentration, agitation speed, and agitation time on the double emulsion stability was carried out. The formulation of ELM on succinic acid separation system was based on Jusoh et al. (2016a) that using Amberlite LA2 as a carrier, palm oil as a diluent, Span 80 and Tween 80 as surfactant, and Na_2CO_3 as a stripping agent.

2. Methodology

2.1 Materials

Palm oil as diluent is ordinary cooking oil (BURUH) from Lam Soon Edible Oils. Amberlite LA-2 as carrier was purchased from MERCK. Solid sodium carbonate (Na_2CO_3) (99 % assay) used as internal solution was obtained from Merck. Sorbitan monooleate (Span 80) and polyoxyethylenesorbitan monooleate (Tween 80) is used as surfactant and purchased from Sigma Aldrich. Succinic acid (SA) (99.0 % assay) was procured from Sigma Aldrich. The reagents and solutions were used directly as received without further purification.

2.2 Emulsion stability study

The double emulsion was prepared using a two-step procedure, consist of preparation of primary emulsion and dispersion process. 10 mL of emulsion prepared (Jusoh et al., 2016b) was dispersed into 30 mL of succinic acid solution as external aqueous phase containing 0 to 3 % (w/v) Tween 80. The external feed phase was stirred using a digital mixer system (Cole-Parmer EW-50006-00, Germany) at agitation speed (200 – 500 rpm) for 1 to 7 min agitation time The range of the operating conditions were determined according to research reported by Othman et al. (2006). Upon completion of agitation, the emulsion was allowed to separate in a separating funnel. A small drop of emulsion was taken and placed under the microscope (Olympus CX31, Japan) to access the state of aggregation of the emulsion globules. The external aqueous phase at the bottom of the funnel was transferred into a measuring cylinder and the volume was recorded. The condition for emulsion dispersion parameters for each experiment are summarised in Table 1. Breakage percentage was calculated based on the volume of internal phase leakage to the external phase as shown in Eq(1).

$$\text{Breakage percentage (\%)} = \frac{V_{e,f} - V_{e,i}}{V_{int}} \times 100\ \% \quad (1)$$

Where $V_{e,f}$ is the volume of external phase after extraction, $V_{e,i}$ is the volume of external phase before extraction, and V_{int} is the volume of internal phase. The final concentration of succinic acid in the external phase was analysed to determine the extraction performance.

Table 1: Dispersion condition for double emulsion stability study

Dispersion parameters	Range
Effect of Span 80 concentration (% w/v)	1, 3, 5, 7
Effect of Tween 80 concentration (% w/v)	0, 1, 2, 3
Effect of agitation speed (rpm)	200, 300, 400, 500
Effect of agitation time (min)	1, 3, 5, 7

3. Results and discussion

3.1 Effect of Span 80 concentration

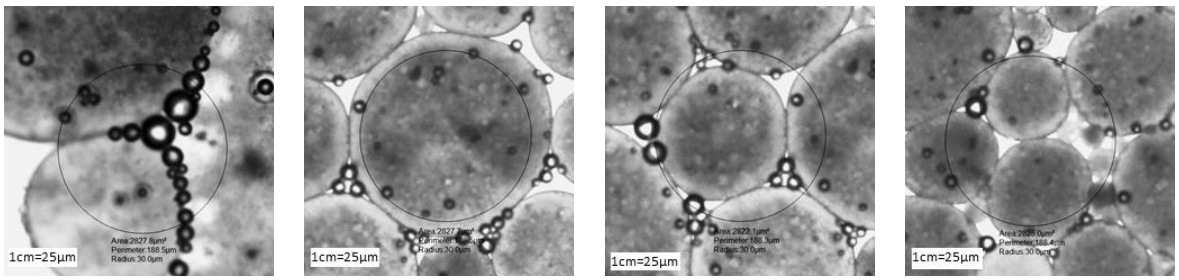
The effect of Span 80 concentration on the W/O/W emulsion stability was studied in the range of 1 – 7 % (w/v) and the result obtained is shown in Table 2. Increase the Span 80 concentration from 1 to 5 % resulted in better stability, where the emulsion breakage recorded was reduced from 80 to 10 %. At low Span 80 concentration, the coverage of Span 80 on the interface is incomplete due to insufficient surfactant. This lack of surfactant causes high surface tension, leading to difficult dispersion and rapid coalescence of emulsion globules. Figure 1a shows larger globules was observed as a result of rapid emulsion coalescence. A smaller globule size in Figure 1b and 1c was formed as a result of lowered interfacial tension at a higher surfactant concentration. Consequently, the interfacial film strength is increased and enhanced kinetic stability of emulsion globules against coalescence. A further increase of Span 80 concentration to 7 % (w/v) resulted in poor W/O/W stability where 40 % of emulsion breakage was observed. It is due to the rapid coalescence of smaller emulsion globules owing to the decrease in interfacial tension at high Span 80 concentration as shown

in Figure 1d. The excess of Span 80 tends to form surfactant aggregates in the liquid membrane phase. These aggregates promote water transport between two aqueous phases and cause breakage (Chaudhuri and Pyle, 1992). Othman et al. (2006) reported that instability of emulsion with increase in surfactant concentration due to Ostwald ripening of emulsion droplets, which in turn leads to increase in swelling and leakage. 5 % (v/w) of Span 80 was chosen in this study to form a stable W/O/W emulsion.

*Table 2: Effect of Span 80 concentration on W/O/W emulsion stability**

% Span 80 (w/v)	% Breakage
1	80
3	60
5	10
7	40

*diluent: palm oil; [Amberlite LA2]: 0.05 M; [Na_2CO_3]: 0.5 M; O/I: 3/1; homogeniser speed: 7,000 rpm; emulsifying time: 5 min; Tween 80: 0 %; agitation time: 3 min; agitation speed: 300 rpm



a) 1 % b) 3 % c) 5 % d) 6 %

Figure 1: Microscopic image of emulsion at different Span 80 concentration at 10 mins (magnification 400x)

3.2 Effect of Tween 80 concentration

A mixture of two surfactants may be needed to obtain better emulsion stability, usually one with a low HLB to stabilise the W/O interface and the other with a high HLB to stabilise the O/W interface (Bjorkegren and Karimi, 2012). The chemical composition of the hydrophilic surfactant also influence the properties of W/O/W emulsions. The hydrophilic surfactant must be compatible with the oil phase and the properties of the lipophilic surfactant (Span 80) (Schmidts et al., 2009). With respect to Span 80 with HLB 4.3, emulsions were prepared by mixing polyethoxylated ethers (Tween 80) with HLB of 15 and the effects of different Tween 80 concentrations are shown in Table 3 and Figure 2. The addition of 1 % Tween 80 in the external phase enhances the emulsion stability where no breakage was observed compared to 0 % Tween 80 with 10 % breakage. This is due to Tween 80 migrated to the external O/W interface, further reducing interfacial tension and facilitated the second emulsification. The result is supported with Figure 2b where more emulsion globules with smaller size were formed compared to Figure 2a. The stability of W/O/W also improved due to Tween 80 minimise the repulsion of the hydrophilic head group of Span 80, which contributes to a more efficient packing of the surfactants at the interface, owing to the similar structure between both surfactant, since Tween 80 is a derivative from Span 80.

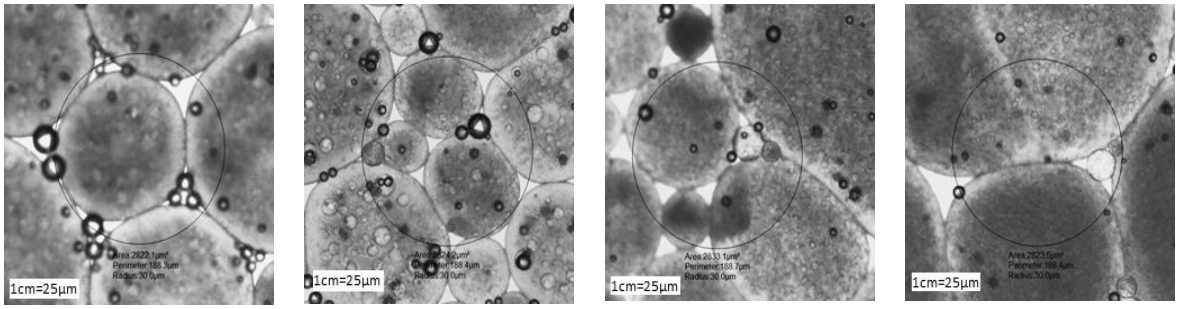
*Table 3: Effect of Tween 80 concentration on W/O/W emulsion stability**

% Tween 80 (w/v)	% Breakage
0	10
1	0
2	20
3	40

*diluent: palm oil; [Amberlite LA2]: 0.05 M; [Na_2CO_3]: 0.5 M; O/I: 3/1; homogeniser speed: 7,000 rpm; emulsifying time: 5 min; Span 80: 5 %; agitation time: 3 min; agitation speed: 300 rpm

With a further increase of Tween 80 concentration to 2 % and 3 %, the emulsion stability was reduced and led to emulsion breakage. This is attributed to the formation of micelles of Tween 80 at high concentration, which may solubilise the Span 80 from liquid membrane phase (Karjiban et al., 2012) which led to a decrease in

concentration of Span 80 in the liquid membrane phase. As a result, the interfacial surface tension increased and caused membrane breakage and leakage of the internal aqueous phase. This result is in agreement with Jiao and Burgess (2003). 1 % (w/v) Tween 80 concentration was chosen as the best condition to form a stable W/O/W emulsion in this study.



a) 0 % b) 1 % c) 2 % d) 3 %

Figure 2: Microscopic images of emulsion for different surfactant concentration at 10 min (magnification 400x)

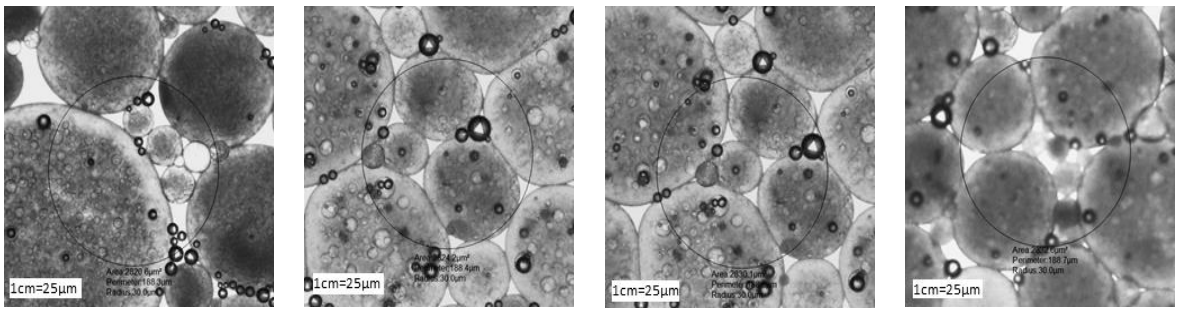
3.3 Effect of agitation speed

The effect of agitation speed in the range of 200 rpm to 500 rpm on W/O/W emulsion stability is presented in Table 4. The emulsion stability increased with agitation speed where 20 % and 0 % of emulsion breakage was observed at 200 and 300 rpm. At low agitation speed, shear energy provided was insufficient to disperse emulsion in the external phase and larger globules was formed as shown in Figure 3a. The globules formed is easy to coalesce and emulsion breakage occurred. A study by Othman et al. (2016) who also reported the formation of large globules at low agitation speed. When the agitation speed is increased from 300 to 500 rpm, the percentage of emulsion breakage also increased significantly. This is due to the emulsions is exposed to high shear and led to the globules rupture and allowed leakage of the internal phase. The microscopic image of the emulsion globule in Figure 3 shows that the size of globule formed was smaller at higher agitation speed. Consequently, this condition caused the thinning of interfacial film and favored rapid coalesce of emulsion globules which led to breakage. The breakage phenomenon is particularly influenced by the impact from the impeller blade which contributed to the turbulent effect on the ELM system. Instability of emulsion at high agitation speed was also reported by Chaouchi and Hamdaoui (2014). The agitation speed of 300 rpm was chosen as the best condition to obtain a stable W/O/W in this study.

*Table 4: Effect of agitation speed on W/O/W emulsion stability**

Agitation speed (rpm)	% Breakage
200	20
300	0
400	20
500	40

*diluent: palm oil; [Amberlite LA2]: 0.05 M; [Na_2CO_3]: 0.5 M; O/I: 3/1; homogeniser speed: 7,000 rpm; emulsifying time: 5 min; Span 80: 5 %; Tween 80: 1 %; agitation time: 3 min



a) 200 rpm b) 300 rpm c) 400 rpm d) 500 rpm

Figure 3: Microscopic image of emulsion for different agitation speed at 10 min (magnification 400x)

3.4 Effect of agitation time

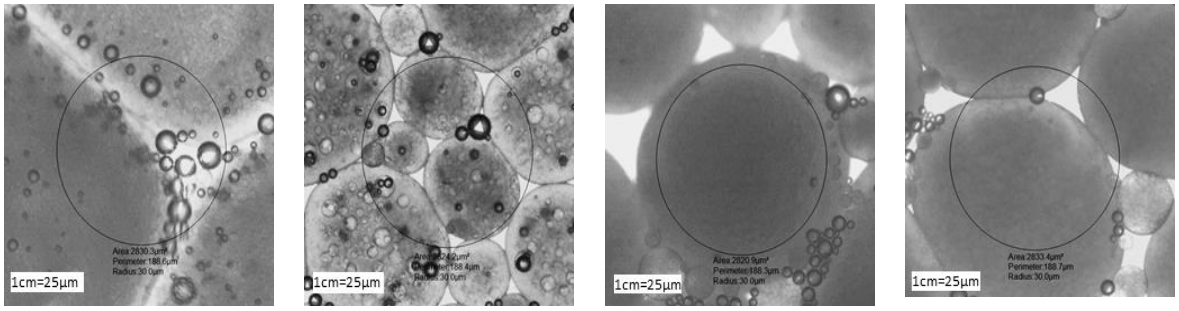
The effect of agitation time on W/O/W emulsion stability is presented in Table 5.

Table 5: Effect of agitation time on W/O/W emulsion stability

Agitation time (min)	% Breakage
1	40
3	0
5	20
7	40

*diluent: palm oil; [Amberlite LA2]: 0.05 M; [Na_2CO_3]: 0.5 M; O/I: 3/1; homogeniser speed: 7,000 rpm; emulsifying time: 5 min; Span 80: 5 %; Tween 80: 1 %; agitation speed: 300 rpm

The results show that emulsion stability was improved when the agitation time is increased from 1 to 3 min where 40 % and no breakage was observed. The breakage was relatively high at a short agitation time due to insufficient time provided for emulsion dispersion and led to the formation of larger size of emulsion globules and easily broken as shown in Figure 4a. Consequently, coalescence phenomenon could occur within a shorter time. The increase in agitation time to 3 min attributed to a more uniform size of globule dispersion, which promoted better stability as shown in Figure 4b.



a) 1 min b) 3 min c) 5 min d) 7 min

Figure 4: Microscopic images of emulsion for different agitation time at 10 min (magnification 400x)

A further increase in the agitation time to 5 and 7 min resulted in poor emulsion stability. The result shows that 20 % and 40 % of emulsion breakage was observed at 5 and 7 min. A longer agitation time favors dispersion of smaller emulsion globules, which led to the coalescence of the globules and caused breakage. Figure 4c and 4d show larger globules were formed at a longer agitation time as a result of globules coalescence. A longer agitation time also resulted in more water transport into the internal phase, which caused the membrane to swell and subsequently initiated breakage of the emulsion phase. Breakage of emulsion phase at longer agitation time was also reported in the ELM process of molybdenum extraction (Kulkarni and Mahajani, 2002). An agitation of 300 rpm was selected to produce a stable W/O/W emulsion.
The best process conditions to produce high stability of W/O/W emulsion without emulsion breakage are summarised in Table 6. At this condition, 70 % of succinic acid was extracted.

Table 6: Best condition for W/O/W emulsion stability

Parameter	Best condition	% succinic acid extraction
Span 80 (% w/v)	5	70
Tween 80 (% w/v)	1	
Agitation speed (rpm)	300	
Agitation time (rpm)	3	

4. Conclusions

The results of this study show that all parameters have a significant effect on the stability of double emulsion. The best condition for stable emulsion for succinic acid extraction was observed at 5 % (w/v) of Span 80, 1 % (w/v) of Tween 80, 300 agitation speed, and 3 min of agitation time. According to the result, there was no breakage observed during the agitation process and suitable to perform the extraction process.

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