RESEARCH ARTICLE

Empirical Correlation of Stable Double Emulsion System of Organic Compound Extraction in Emulsion Liquid Membrane Process

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Abstract The stability of emulsion is crucial in the emulsion liquid membrane (ELM) process. It has been discovered that the size of emulsion droplets and globules is related to ELM stability and can be predicted using a correlation model. In this study, an empirical equation for the prediction of emulsion size in ELM extraction of succinic acid was developed. The accuracy of the correlation was compared with other established correlations at several affecting parameters including emulsification speed, emulsification time, agitation speed, and treat ratio. A new correlation for the succinic acid system was obtained that fit experimental data between 0.1-0.5 dispersed phased holdup fraction ϕ, which is $\frac{D_{32}}{D_I} = 0.0868(1 - 1.1071\phi)We^{-0.6}$ (where D_{32}, D_I, and We is Sauter mean diameter, impeller diameter, and Weber number, respectively). From the study, the Weber number depended on the emulsification speed, emulsification time, and agitation speed, which consequently affected the predicted emulsion size. This study demonstrates that mathematical correlations can be used to predict the size of emulsion droplets and globules in the ELM process of organic compound extraction.

Keywords: correlation, emulsion liquid membrane, stability, succinic acid.

Introduction

Nowadays, the versatility of liquid membrane technology in the separation process has been recognized. This technology offers various advantages such as low capital and operating costs, simplicity, high diffusion rate due to large mass transfer area, and low energy consumption [1, 2]. The main categories of this system are bulk liquid membrane, supported liquid membrane, and emulsion liquid membrane.

Emulsion liquid membrane (ELM) consists of three liquid phases (external, liquid membrane, and internal). It can carry out the stripping and extraction process simultaneously. The ELM has more advantages over any other separation technique as it consumes low energy, has high efficiency for extraction, and is time-saving. The properties of the dispersed and continuous phase determine the emulsion type. This composition contains organic material and a stripping agent. There are two types of emulsion which are primary emulsion and double emulsion. The primary emulsion can be either oil-in-

water (O/W) emulsion or water-in-oil (W/O) emulsion that is produced from the dispersion of the internal phase in the liquid membrane phase. An amphiphilic molecular structure (containing lipophilic and hydrophilic parts) called a surfactant is required to create the emulsion.

Meanwhile, the double emulsion can be an oil-in-water-in-oil emulsion (O/W/O) or water-in-oil-in-water emulsion (W/O/W). The double emulsion is formed by the dispersion of the primary emulsion in the external phase. The ELM has been applied in the formulation of pharmaceuticals including drug carries in blood substitute, vaccines, enzymes, and vitamins [3]. Besides that, the ELM has been studied for various applications such as metal extraction, bio-medical separation, removal of acid, and metal recovery [4-6]. Therefore, the design for the ELM is modified according to the specifications and the aimed applications.

Despite that, there are many obstacles to the ELM process which are the stability of the emulsion system which can cause breakage and de-emulsification. The emulsion is considered stable if there is no breakdown recorded within 24 hours. In order to produce a stable emulsion, it is important to have a deeper understanding about the stability of the emulsion system and how to preserve the stability of the emulsion from breaking down [7]. This is difficult to maintain in the liquid membrane process, so the stability of the emulsion is crucial to determine the efficiency of the ELM system. Previous research shows that correlation can be established between the ELM stability and size of emulsion droplets and globules depending on several factors during the formation of primary emulsion and emulsion dispersion.

Jahanzad et al. [8] studied the relationship between particle size and monomer-water dispersion in suspension polymerization. The results showed that during the early transition stage in suspension polymerization, the viscosity of the emulsion was sufficient to increase the steady-state droplets size. Based on the finding, the stability of drop size increases with initiator concentration and temperature. Meanwhile, the decrease in initial concentration, temperature, holdup fraction, as well as the increase in stabilizer concentration and agitation speed resulted in higher emulsion breakage. Therefore, a good correlation (statistical term describing the relationships between variables) was found between the parameters investigated and the droplet size [8]. Wang and Calabrese [9] also established the correlation equation that relates to the stability of the ELM system. The influence of dispersed phase viscosity on droplet size distribution at constant interfacial tension was examined. Besides that, the study also presented the range of applicability of the semi-empirical theory and the relevance of the predicted correlating parameters [9].

Previously, primary W/O and double W/O/W emulsion stability for the extraction of succinic acid have been studied [10, 11]. However, a correlation that represent the relationship between the parameter investigated and emulsion size has yet been established. In this research, a new correlation is proposed to predict the emulsion droplet and globule size for the ELM extraction of succinic acid. Notably, different mathematical correlation also depends on the impeller type and tendency of droplet coalescence [12]. Therefore, the new correlation was compared with the experimental data and the data calculated from correlation by Jahanzad et al. [8] and Wang and Calabrese [9] that was developed using same type of system which is flat blade impeller system.

Materials and methods

Correlation Equations
Most of the correlations for determining Sauter mean diameter of the emulsion droplets were developed according to Hinze-Kolmogorov's theory as presented in Equation 1 [13].

$$\frac{D_{32}}{D_I} = C_1(1 + C_2\phi)We^{-0.6} \tag{1}$$

where D_{32} is Sauter mean diameter, D_I is the impeller diameter, C_1 and C_2 are constant, ϕ is the holdup or dispersed phase fraction, and We is Weber number. The Weber number is dimensionless. For this case, the Weber number which is affected by the emulsification apparatus and often used to scale up at

geometric similarity is defined by Equation 2:

$$We = \frac{\rho_c N^2 D_I{}^3}{\sigma} \tag{2}$$

where ρ_c is the density of the continuous phase, N is the impeller speed, and σ is the interfacial tension.

For correlation by Jahanzad et al. [8], the holdup volume fraction that varied between 0.05 and 0.4 can be fitted into their correlation as shown in Equation 3:

$$\frac{D_{32}}{D_I} = 0.022 \, (1 + 3.55 \, \phi) We^{-0.6} \tag{3}$$

Furthermore, Wang and Calabrese [9] also used the Weber number by considering emulsification speed and emulsification time as the parameters. That affects the correlation for the prediction size of the droplets and globules as shown in Equation 4:

$$\frac{D_{32}}{D_I} = 0.066 We^{-0.66}[1 + 13.8 Vi^{0.82}\left(\frac{D_{32}}{D_I}\right)^{0.33}]^{0.59} \tag{4}$$

Wang and Calabrese [9] introduced the viscosity vessel number, Vi in the correlation above. The holdup volume fraction was less than 0.002 and therefore the holdup was neglected in the correlation. The correlation is valid for the viscosity of dispersed phase, µd<0.5 Pa.s where it was applied in the viscosity vessel number as shown in Equation 5:

$$Vi = \frac{\mu_d N D}{\sigma}(\frac{\rho_c}{\rho_D})^{1/2} \tag{5}$$

where, ρ_D is the density of the dispersed phase and ρ_C is the density of the continuous phase. All these correlations were established by using a flat blade impeller system and were used to compare with the experimental data work.

The Sauter mean diameter obtained from previous experimental data was compared with the Sauter mean diameter from the correlations proposed in order to evaluate the average absolute relative deviation (AARD) or the percentage error as shown in Equation 6:

$$AARD = \frac{1}{NE}\sum_{l=1}^{NE}|\frac{(D_{32})i,exp-(D_{32})i.calc}{(D_{32})i,exp}| \tag{6}$$

where, $(D_{32})i, exp$ is the measured Sauter mean diameter, $(D_{32})i.calc$ is the calculated Sauter mean diameter from the proposed correlation and NE is the number of experimental data points. The best correlation was selected to predict the size of droplets and globules for both primary and double emulsion.

Dispersed Phase Holdup
The dispersed phase holdup was calculated using volume displacement method as shown in Equation 7. The holdup volume fraction has a high effect on the correlation.

$$\phi i = \frac{V_d}{V_d + V_o} \tag{7}$$

where V_d represents the volume of dispersed phase and V_o represent the volume of the organic phase. Equation 7 is known as internal droplet fractions and is valid to the primary emulsion only. Meanwhile, for the double emulsion, one more phase will be added and arranged to form Equation 8 below:

$$\phi_g = \frac{V_d + V_o}{V_d + V_o + V_f} \tag{8}$$

where V_d represents the volume of the dispersed phase, V_o represents the volume of the organic phase, and V_f represents the volume of feed or external phase or in this research, water solution is used.

Results and discussion

Development of empirical equation

The actual Sauter mean diameter of emulsion from a previous study for succinic acid extraction [14] was compared with the Sauter mean diameter from the correlation. A new correlation was introduced based on the general equation developed by the Hinze theory in Equation 1. The experimental value of D_{32} at different dispersed phased holdups was applied in the equation and the constant value obtained was $C_{1=}-0.0868$ and $C_2 = -1.1071$ as shown in Equation 9. The experimental data and predicted value using a new correlation are shown in Figure 1. According to the results, the correlation data were fitted on the experimental data, with a small AARD value of 3.3%. The accuracy of this correlation in predicting emulsion size by varying several parameters are discussed in the following section.

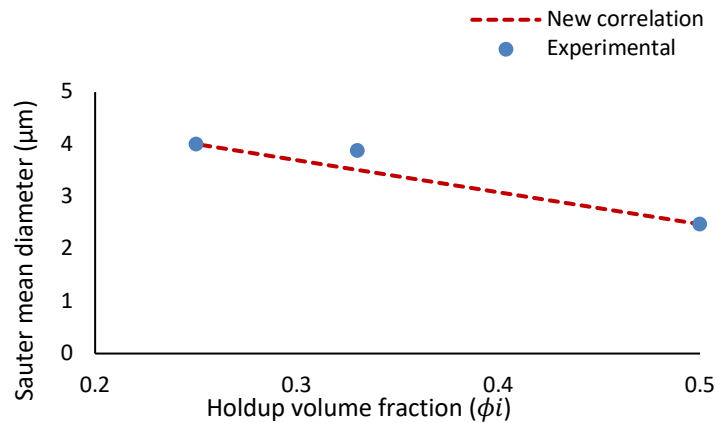$$\frac{D_{32}}{D_I} = 0.0868(1 - 1.1071\phi)We^{-0.6} \tag{9}$$

Figure 1. Actual and predicted Sauter mean diameter (D_{32}) of emulsion.

Effect of emulsification speed

Emulsification is the key to the formation of primary emulsion (W/O) and the speed affects the emulsion droplet size. The effect of emulsification speed on the size of emulsion is presented in Table 1. The results show that at a lower emulsification speed, a larger droplet size was produced which is 2.40 µm. This is due to insufficient energy to break down the emulsion, thus resulting in larger droplets. This induced a faster rate of emulsion breakage and destabilized the emulsion. The increased emulsification speed from 7000 rpm produced a smaller droplet (2.25 µm). This is due to the higher mechanical energy provided that increased the water-oil interface and produced a higher number of smaller aqueous droplets, thus stabilizing the emulsion. A similar trend was also found for the stability of phenol extraction [15]. With a further increase of emulsification speed to 12000 rpm, the size of the droplets was reduced to 2.12 µm. However, a very viscous, "mayonnaise-like" emulsion was formed [14]. This result is likely to be related to the foaming mechanism, where the air bubbles are combined into the emulsions phase, resulting in a rigid system.

Table 1. Effect of emulsification speed on Sauter mean diameter of emulsion droplets.

Emulsification speed (rpm)	Droplet size (µm)
7000	2.40
9000	2.25
12000	2.12

Meanwhile, Figure 2 presents the actual and calculated size of emulsion droplets at different emulsification speeds. For experimental data and other correlations, the Sauter mean diameter of the emulsion droplet shows a decreasing trend with emulsification speed. This is due to an increase of emulsification time that led to the increase of the Weber number and thus reduced the value of the calculated Sauter mean diameter. Meanwhile, it can be seen from the graph that the new correlation most fitted with the experimental data and the AARD value was 9.2%, followed by Jahanzad et al. [8] (11.6% AARD) and Wang and Calabrese [9] (27.8% AARD) correlations.
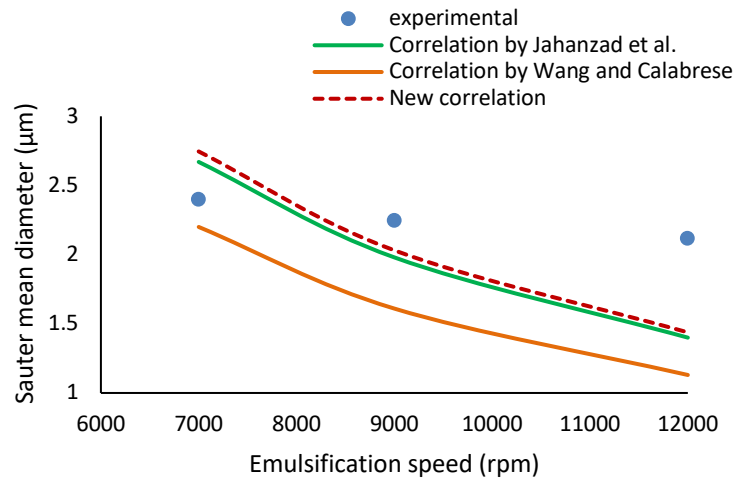

Figure 2. Actual and calculated droplet size at different emulsification speed for the extraction of succinic acid

Effect of emulsification time

Another important parameter to ensure a uniform droplet formation and a stable emulsion is emulsification time. Table 2 provides the emulsion droplet size distribution at different emulsification times. At a shorter emulsification time, larger droplets were formed (11.2 µm) due to insufficient time provided for the homogenization of organic and internal phases. As reported by Gaikwad and Pandit [16], larger droplets have a tendency to coalesce with one another and cause unstable emulsion. Besides that, a shorter time was also insufficient for the surfactant to engage at the oil-water interface, causing disordered surfactant configuration. Consequently, a weak and fragile membrane layer was formed, leading the membrane to rupture easily.

An increment to the emulsification time formed a smaller emulsion which was 4.90 µm. This led to a more stable system as smaller droplets take more time to coalesce and reduce the breakage rate [17]. However, a longer emulsification time (10 minutes) causes unstable emulsion and a larger emulsion droplet (8.30 µm). The result is in line with Othman et al. [18] who stated that prolonged emulsification time induced the breakage phenomenon and unstable emulsion. In addition, Abedi et al. [19] stated that emulsions that have larger droplet sizes are less stable than the emulsions of smaller droplets as the tendency to initiate coalescence is lower.

Table 2. Effect of emulsification time on Sauter mean diameter of emulsion droplets.

Emulsification time (minute)	Droplet size (µm)
3	11.20
5	4.90
10	8.30

The comparison between the experimental data and correlation value for emulsion droplet size at different emulsification times is shown in Figure 3. Basically, the Weber number increases with emulsification time. Therefore, the predicted Sauter mean diameter showed a decreasing trend. However, the result at 10 minutes of emulsification time showed a different trend from the experimental owing to the emulsion instability. Since breakage phenomenon was not considered in the correlation, the value of AARD at 10 minutes emulsification time was excluded. Based on the result, the data for all correlations deviated from the experimental data with the AARD value of 32.9%, 33.8%, and 38.2% for new, Jahanzad et al. [8], and Wang and Calabrese [9] correlations, respectively.
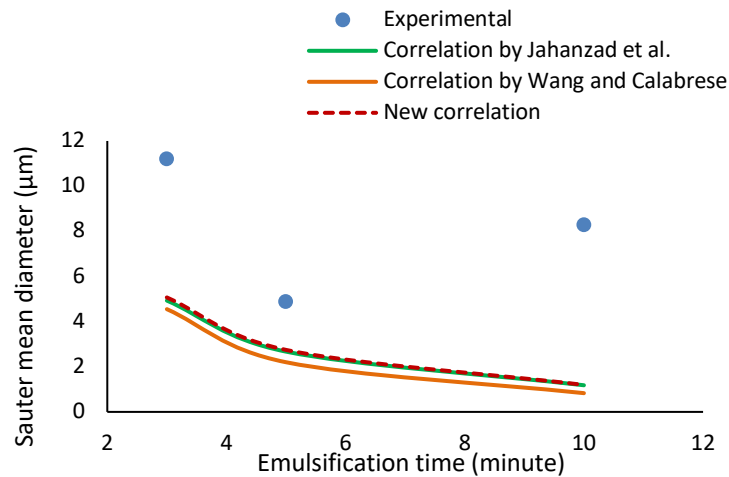

Figure 3. Actual and calculated droplet size at different emulsification time for the extraction of succinic acid.

Effect of agitation speed
The agitation speed in the ELM system affects the size distribution of the emulsion globules. The speed was varied from 200 to 500 rpm and the results are shown in Table 3. It can be seen that the size of emulsion globules decreased with agitation speed. At 200 rpm, larger globules were formed (52.67 µm) owing to insufficient energy provided to break the emulsion. Consequently, the globules formed was easy to coalesce and become unstable [20]. Smaller emulsion globules (36.48 µm) were formed when the agitation speed was increased to 300 rpm. This helps to prevent the emulsion globules from coalescing, resulting in a more stable system. By increasing the agitation speed to 500 rpm, smaller emulsion globules were formed (17.66 µm). However, the emulsion was reported to be unstable due to the thinning of the liquid membrane layer that encouraged rapid coalescence of emulsion globules [14]. Another study by Lee and Hyun [21] also reported that the increasing speed beyond a certain limit will lead to the globules rupturing.

Table 3. Effect of agitation speed on Sauter mean diameter of emulsion globules.

Agitation speed (rpm)	Globule size (µm)
200	52.67
300	36.48
500	17.66

Figure 4 shows the comparison of emulsion globules size between the experimental and correlation value at different agitation speeds. The trend for emulsion globule size is similar for the actual and calculated value using all correlations. This is owing to the Weber number that increases with agitation speed, thus reducing the globule size. For this system, the predicted globule size using correlation by Wang and Calabrese [9] closely fitted with the experimental value (7.5% AARD), followed by Jahanzad et al. [8] (22% AARD) and new correlation (24% AARD)

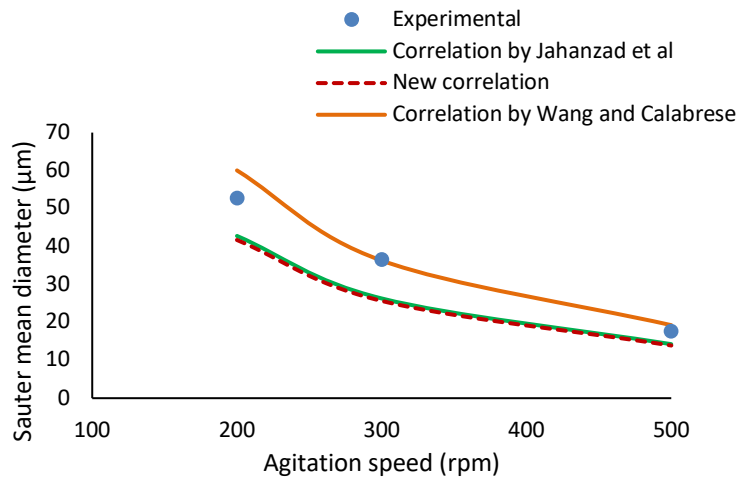**Figure 4.** Actual and calculated globule size at different agitation speed for the extraction of succinic acid.

Effect of treat ratio

Treat ratio represents the ratio (by volume) of the primary emulsion to the external phase that needs to be varied so that a stable ELM system can be achieved. The effect of treat ratio on emulsion globules size for extraction of succinic acid is displayed in Table 4. At the treat ratio of 1:3, a larger globule size was observed (25.64 µm). This is owing to the effect of osmotic pressure that resists the production of emulsion globules in the external phase. The smaller size of the emulsion globule was observed at the treat ratio of 1:5 and 1:7 which were 23.70 µm and 18.03 µm, respectively. The result is likely to be related to the better dispersion of emulsion in a larger external phase volume.

Table 4. Effect of treat ratio on Sauter mean diameter of emulsion globules.

Treat ratio	Globule size (µm)
1:3	25.64
1:5	23.70
1:7	18.03

The comparison of actual and predicted globule size at different treat ratios is shown in Figure 5. A higher volume of external phase reduces the dispersed phase holdup value fraction, thus reducing the predicted globule size. From the graph, the experimental and predicted globule size shows a decreasing trend, indicating the correlation is reliable to predict the emulsion globules. In addition, the AARD value for both correlations is acceptable which is 0.3% and 4.5% for Jahanzad et al. [8] and the new correlation, respectively. Meanwhile, the correlation by Wang and Calabrese [9] was not considered since the holdup volume fraction was neglected in the correlation.
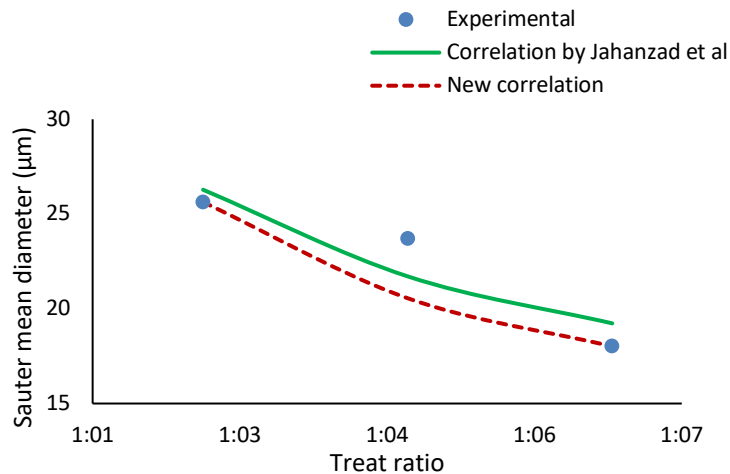
Figure 5. Actual and calculated globule size at different treat ratios for the extraction of succinic acid.

Conclusions

Prediction of emulsion droplet and globule size for emulsion stability can be made by correlations at different parameters. A new correlation for the succinic acid system was obtained that fit experimental data between 0.1-0.5 dispersed phased holdup fraction, which is $\frac{D_{32}}{D_I} = 0.0868(1 - 1.1071\phi)We^{-0.6}$. The average AARD for all the parameters studied were 17.6, 16.9, and 24.5 for new, Jahanzad et al. [8], and Wang and Calabrese [9] correlations, respectively. From the study, the Weber number is depended on the emulsification speed, emulsification time, and agitation speed, which consequently affected the emulsion size.

Conflicts of interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Funding statement

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