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Vegetable Oil–Ionic Liquid-Based Emulsion Liquid Membrane for the Removal of Lactic Acid from Aqueous Streams: Emulsion Size, Membrane Breakage, and Stability Study

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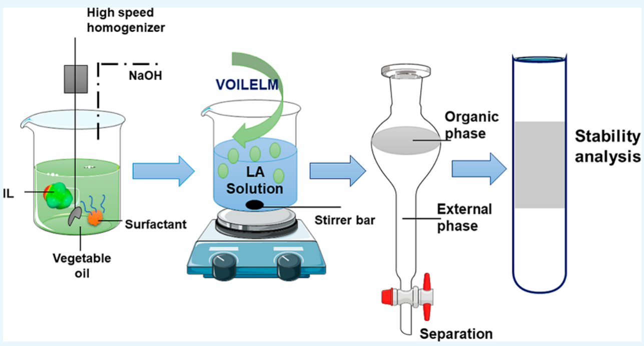
ABSTRACT: In this study, we present a highly stable vegetable oil ionic liquid (IL)-based emulsion liquid membrane (VOILELM) for the removal of lactic acid from water streams. The system developed as a part of this work comprises a non-ionic surfactant Span 80, sodium hydroxide as an internal stripping agent, sunflower canola oil as a green diluent, and IL—tetramethylammonium acetate [TMAm][Ac]—as a carrier. VOILELM stability was evaluated in terms of breakage, emulsion diameter, and standalone stability. The effect of various parameters, namely, concentration of the surfactant, concentration of the internal stripping agent, concentration of the carrier, phase ratio, homogenizer speed, and homogenization time, on the VOILELM stability was studied. The results revealed that VOILELM was highly stable, with 1.34% minimum breakage, 1.16 μm emulsion diameter, and 131 min standalone stability. The optimal process parameters were 0.1 wt % Span 80, 0.1 M NaOH, 0.3 wt % IL, 0.25 phase ratio, 5000 rpm homogenizer speed, and 5 min homogenization time. At these optimized conditions, 96.08% lactic acid extraction efficiency was achieved. Thus, a highly effective VOILELM was developed, with minimal breakage and emulsion diameter and maximum stability.



1. INTRODUCTION

Biologically active compounds (BACs) are emerging contaminants in aqueous streams. When these compounds reach water bodies, due to their biologically active nature, they undergo further reactions, giving rise to harmful compounds that are more hazardous than their parent compounds. Owing to their toxic nature and environmental constraints, these compounds need to be separated from aqueous streams. At present, lactic acid (LA) is one of the most commonly discharged BACs into aqueous streams, as it is widely used in the pharmaceutical industry and is frequently found in fermentation broths.[1] In addition, LA is an active ingredient of many personal care products.[2] Because of the increasing demand for LA, its recovery from aqueous streams is becoming highly important. Various extraction methods, including solvent extraction,[3] ultrafiltration,[4] nanofiltration membrane,[5] membrane reactor,[6] and adsorption,[7] have been applied for the removal of LA from water streams. Despite their widespread use, the aforementioned methods often suffer from drawbacks such as low extraction efficiencies and the employment of organic solvents that are extremely hazardous to the environment. Liquid membrane technology (LMT) can overcome many of these challenges. In particular, emulsion liquid membranes (ELMs) have been successfully used in the separation of BACs,[8] heavy metals,[9] and organic compounds[10] due to their various advantages such as facile process design and high efficacy.[2]

An ELM is also termed "double membrane" as it involves the formation of emulsion (water-in-oil), which is dispersed into another medium, forming another emulsion (water-in-oil-in water).[11] The ELM possesses several advantages, such as solute extraction even in minute quantities, high interfacial area,[12] and selective separation with high extraction efficiency.[13] However, in most cases, the ELM is insufficiently stable and requires a large amount of petroleum-based volatile organic solvents.[14] Membrane stability also depends on its composition, the shear produced by agitation, and the internal emulsion diameter.[15] Emulsion instability is another issue, resulting from the membrane breakage and thus causing leakage of the internal aqueous phase into the external phase.[16]

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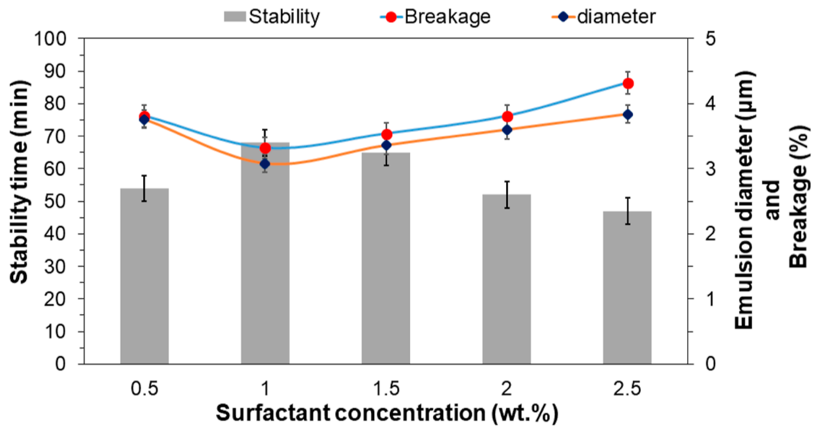

Figure 1. Effect of the concentration of the surfactant on the standalone stability, emulsion diameter, and breakage. Experimental conditions: SFO: 10 mL, NaOH concentration: 0.1 M, [TMAm][Ac] concentration: 0.3 wt %, phase ratio: 0.25, homogenization speed: 5200 rpm, homogenization time: 5 min, treat ratio: 3, stirring speed: 270 rpm, stirring time: 20 min, and settling time: 5 min.

ELM instability can also occur when the water molecules enter emulsion, causing it to swell,[17] which decline the extraction efficiency.[18] Therefore, ELM stability can be improved by adding an external agent termed "carrier".[19] Conventional carriers employ organic solvents, including di(2-ethylhexyl) phosphoric acid (D_2EHPA),[20] trioctylamine (TOA),[21] and so forth. To overcome the well-known problems associated with organic solvents such as toxicity, non-biodegradability, and environmental pollution, ionic liquids (ILs) are increasingly being employed as environmentally friendly, or greener, alternatives.[22]

ILs, new "green solvents", are well recognized in separation technologies.[23] ILs are also termed "architect solvents" as they can be modified to meet the application requirements and match the solute type.[24] As ILs have been found very effective in the separation process, they are employed in wastewater treatments based on extraction processes.[25] Recently, ILs have also been used as carriers in an ELM, especially those utilizing trioctylmethylammonium chloride [TOMAC],[26] 1-butyl-3-methyl imidazolium bistriflurosulfonylimide [BMIM][Ntf_2],[27] and tetramethylammonium bromide [TMAm][Br].[28] Since thousands of ILs are available, and data on ILs are scarce,[29] experimentally selecting an IL for the target molecule is difficult.[22] Thus, a conductor-like screening model for real solvents would be an ideal approach for the selection of an effective IL.[22,24] With the introduction to sustainable development goals (SDGs),[30] green innovative practices (GIPs)[31]—and thus more environmentally friendly diluents—need to be explored.[32] Vegetable oils are a suitable alternative for use in greener ELM development.

In our previous study, optimization was carried out using three ILs: tetramethylammonium acetate [TMAm][Ac], tetramethylammonium chloride [TMAm][Cl], and tributylmethylammonium chloride [TBMAm][Cl]. Our findings indicated that [TMAm][Ac] was the most effective carrier in terms of its LA extraction efficiency.[2] Despite the fact that the extraction efficiencies of all the three ILs were tested and a full analysis was conducted, the stability, which is the governing element for an efficient ELM, was not investigated at the time.

Therefore, the main objective of this work was to study the stability and effects of various parameters on the stability of vegetable oil IL-based emulsion liquid membrane (VOILELM). Stability measurements were in terms of standalone stability (min), breakage (%), and emulsion diameter (μm). VOILELM was formulated using an IL screened through COSMO-RS. In our previous study, 120 IL combinations were screened for their potential use as carriers in the ILELM development. The results revealed that acetate-based quaternary ammonium ILs would be particularly effective carriers.[22] To achieve this goal, in the present study, 100% vegetable oil (namely, sunflower canola oil blend) was used as the green diluent, Span 80 as a non-ionic surfactant, and NaOH as an internal stripping agent, while tetramethylammonium acetate [TMAm][Ac] was selected as the IL, in line with our previous findings.[22] As the emulsion stability mainly depends on its composition and emulsification conditions, various parameters that affect the emulsion formulation and emulsification were investigated in this research, namely, the surfactant concentration, the internal stripping agent concentration, the IL concentration as the carrier, phase ratio, homogenization speed, and homogenization time. In sum, the main objective of this research was to explore the resulting ELM stability.

2. RESULTS AND DISCUSSION

2.1. Effect of the Surfactant Concentration on VOILELM Stability. Generally, an adequate amount of surfactant is required for the formulation of stable VOILELM. The surfactant reduces the interfacial tension and increases the emulsion stability.[33] The effects of different concentrations of the surfactant on the breakage, emulsion diameter, and standalone stability of VOILELM are present in Figure 1. As can be observed from the graph, VOILELM was initially highly unstable, and the breakage was relatively high (3.81%). However, as the surfactant concentration increased, the VOILELM standalone stability improved. At 1 wt % surfactant concentration, 68 min stability was achieved, with a minimum breakage of 3.08% and an emulsion diameter of 3.32 μm. However, the viscosity increased with a further increase in the surfactant amount. This is because an excess surfactant concentration results in the formation of aggregates, causing an increase in viscosity. As a result, the emulsion diameter and breakage increased, rendering VOILELM unstable. Therefore, 1 wt % of the surfactant was selected for the development of VOILELM. Similar observations were reported in our previous study which focused on lactic acid extraction.[2] Also, similar results were reported in a previous work upon lactic acid extraction where 2 wt % of Span 80 was adequate for the formulation of an ELM.[34]

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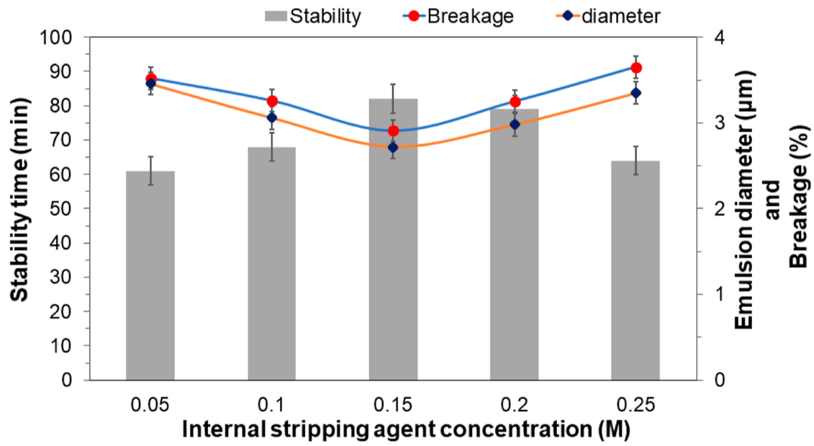

Figure 2. Effect of the concentration of the internal stripping agent on the standalone stability, emulsion diameter, and breakage. Experimental conditions: SFO: 10 mL, Span 80 concentration: 1 wt %, [TMAm][Ac] concentration: 0.3 wt %, phase ratio: 0.25, homogenization speed: 5200 rpm, homogenization time: 5 min, treat ratio: 3, stirring speed: 270 rpm, stirring time: 20 min, and settling time: 5 min.

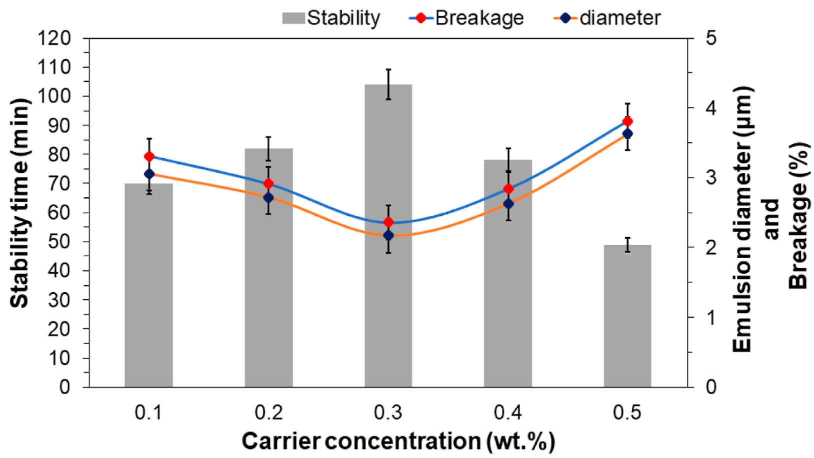

Figure 3. Effect of the concentration of IL as a carrier on the standalone stability, emulsion diameter, and breakage. Experimental conditions: SFO: 10 mL, Span 80 concentration: 1 wt %, NaOH concentration: 0.15 M, phase ratio: 0.25, homogenization speed: 5200 rpm, homogenization time: 5 min, treat ratio: 3, stirring speed: 270 rpm, stirring time: 20 min, and settling time: 5 min.

2.2. Effect of the Internal Stripping Agent Concentration on the VOILELM Stability. As the stripping agent plays a crucial role in the development of a stable VOILELM, the effects of its concentration were investigated. For this purpose, the concentration of NaOH was varied from 0.05 to 0.25 M and the observed impact of these changes on the breakage, emulsion diameter, and standalone stability of VOILELM (Figure 2). It is evident that, at low NaOH concentrations, the emulsion was highly unstable due to larger breakage and emulsion diameter, indicating that the internal stripping agent was insufficient for obtaining a stable VOILELM. With the increase in NaOH concentration, the membrane stability improved as VOILELM was found to be stable for about 80 min at 0.15 M NaOH. Moreover, 2.83% minimum breakage and 2.87 μm emulsion diameter were obtained as a result of greater driving force.[35] However, further increases in the stripping agent concentration resulted in a larger emulsion diameter, increased breakage, and reduced stability, likely as a result of a decline in beneficial surfactant properties. Moreover, an excessive amount of stripping agent induces differences in ionic strength, due to which water molecules start to leak, exacerbating the breakage. Similar results were reported in the literature for acetaminophen extraction.[36] A similar behavior was observed for the extraction of lactic acid where 0.1 N NaOH was found optimum for the development of an effective ELM.[37] Therefore, 0.15 M NaOH was selected as the most optimal stripping agent concentration in this study.

2.3. Effect of the IL Concentration as a Carrier on the VOILELM Stability. A carrier is an essential constituent for VOILELM development as it influences its stability and efficacy.[38] In the present study, tetramethylammonium acetate [TMAm][Ac] was used as a carrier. This particular IL works by forming a complex at the external membrane interphase with the target solute.[39] Furthermore, this complex breaks and forms another complex at the internal phase.[17] (Figure 3) presents the effect of the concentration of IL on the breakage, emulsion diameter, and stability of VOILELM. The results reveal that, without IL, the membrane was highly unstable, with a standalone stability of only 25 min. Moreover, at 5.9%, the breakage was high, and the emulsion diameter was 4.5 μm. After the addition of the IL, the stability markedly improved, as VOILELM was stable for 104 min at 0.3 wt % IL concentration, with a breakage of 2.36%. This finding was expected, as the IL functions by forming complexes, thereby stripping the target molecule, which facilitates regeneration. However, an increase in IL concentration beyond 0.3 wt % resulted in a decrease in VOILELM stability because the

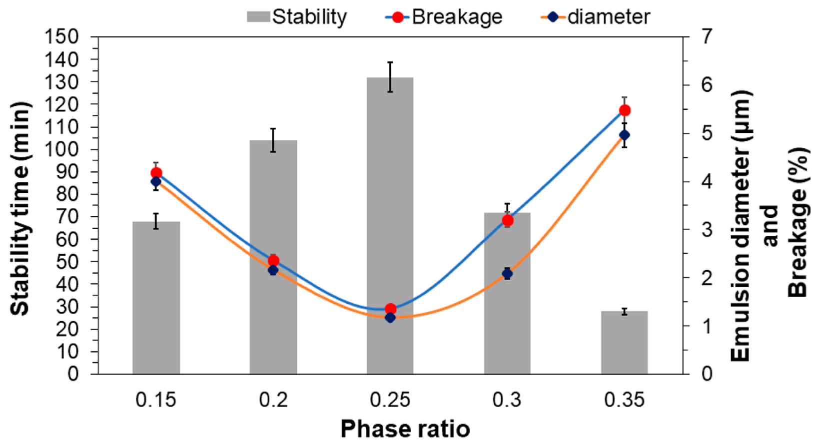

Figure 4. Effect of phase ratio on the standalone stability, emulsion diameter, and breakage. Experimental conditions: SFO: 10 mL, Span 80 concentration: 1 wt %, NaOH concentration: 0.15 M, [TMAm][Ac] concentration: 0.3 wt %, homogenization speed: 5200 rpm, homogenization time: 5 min, treat ratio: 3, stirring speed: 270 rpm, stirring time: 20 min, and settling time: 5 min.

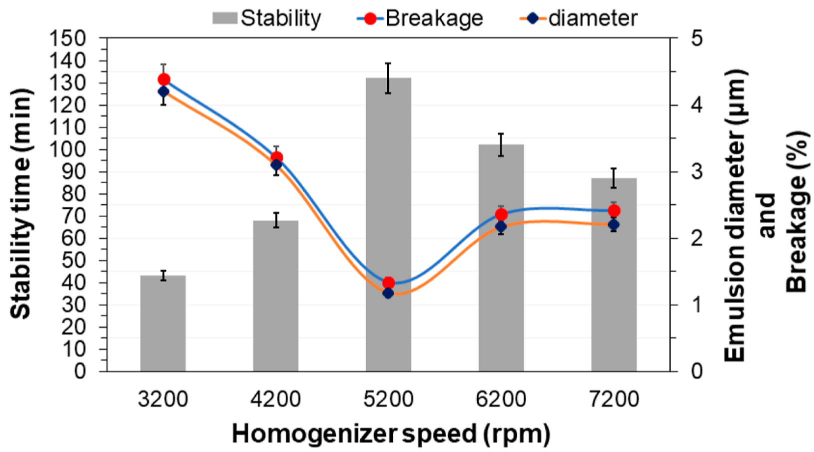

Figure 5. Effect of phase ratio on the standalone stability, emulsion diameter, and breakage. Experimental conditions: SFO: 10 mL, Span 80 concentration: 1 wt %, NaOH concentration: 0.15 M, [TMAm][Ac] concentration: 0.3 wt %, phase ratio: 0.25, homogenization time: 5 min, treat ratio: 3, stirring speed: 270 rpm, stirring time: 20 min, and settling time: 5 min.

membrane viscosity increased, allowing the internal stripping agent to leak into the external phase. The breakage also increased due to which the emulsion diameter increased, compromising the VOILELM stability. In another study using ALIQUAT 336, similar results were found, where 3 wt % of carrier results in a stable ELM for the extraction of lactic acid.[37] These results are in accordance with those obtained previously for the extraction of β-carotene using a quaternary ammonium IL.[40] Hence, in this study, 0.3 wt % of IL was selected for the development of VOILELM.

2.4. Effect of Phase Ratio on the VOILELM Stability. Determining the optimal amount of internal stripping agents is essential for developing a stable VOILELM. The phase ratio indicates the amount of internal stripping agent needed to develop emulsion. Figure 4 depicts the effect of varying the amount of internal stripping agent on the stability, breakage, and emulsion diameter. The results reveal that, when the phase ratio was low, the amount of internal stripping agent was insufficient to form a stable emulsion. As a result, the emulsion diameter was high, giving rise to maximum breakage, whereby the VOILELM was stable for only 68 min. As the phase ratio increased, the VOILELM stability improved and reached 134 min at a phase ratio of 0.25, which corresponded to the lowest emulsion diameter (1.34 μm) and breakage (1.22%). However, a further increase in phase ratio resulted in a larger emulsion diameter, which led to rapid coalescence, reducing the VOILELM stability and increasing the breakage. The main driving force in the ELM process is the difference in hydrogen ion concentration. With an excess phase ratio, the ionic strength increases between aqueous phases and leads to membrane breakage. Similar results were reported for the stability of the ELM for the extraction of lactic acid using rice bran oil as a diluent and NaOH as a stripping agent.[41,42] Therefore, in the present study, the 0.25 phase ratio was selected for VOILELM development.

2.5. Effect of the Speed of the Homogenizer on the VOILELM Stability. Emulsion uniformity is an essential factor for VOILELM stability and the transfer of solute under study, and homogenizer speed governs this parameter.[42] The effect of varying homogenizer speed on the VOILELM breakage, diameter, and stability was thus investigated, and the results are presented in (Figure 5). As observed from the graph, with the increase in homogenizer speed, the emulsion uniformity improved, a homogenous milky white mixture was observed. At 5200 rpm, the emulsion was highly stable for 134 min, and a minimum breakage of 1.22% with a small emulsion diameter of 1.34 μm was achieved. These results were anticipated, as greater homogenizer speed aids in the formation of smaller

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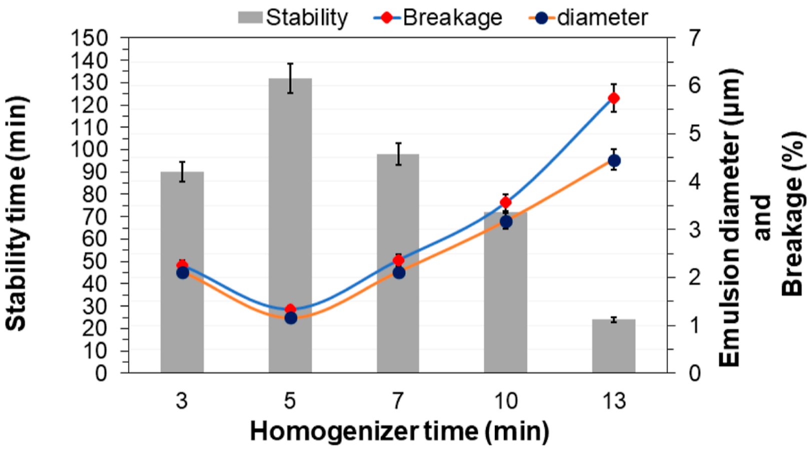

Figure 6. Effect of homogenizer time on the standalone stability, emulsion diameter, and breakage. Experimental conditions: SFO: 10 mL, Span 80 concentration: 1 wt %, NaOH concentration: 0.15 M, [TMAm][Ac] concentration: 0.3 wt %, phase ratio: 0.25, homogenization speed: 5200 rpm, treat ratio: 3, stirring speed: 270 rpm, stirring time: 20 min, and settling time: 5 min.

emulsion globules, resulting in minimal breakage and high stability. However, any further increase in homogenizer speed resulted in an unstable emulsion, as the increased shear[34] causes the formation of emulsion globules that undergo continuous breakage and coalescence, increasing the emulsion diameter. As a result, the internal stripping agent leaks into the external solution, increasing the breakage and decreasing the stability. Similar results were reported for the extraction of lactic acid.[26] A homogenizer speed of 5200 rpm was thus deemed adequate for the development of an effective VOILELM.

2.6. Effect of Homogenization Time on the VOILELM Stability.

The homogenization time directly impacts the emulsion globule size. Determining the optimal homogenization duration is thus necessary for the development of an effective VOILELM. (Figure 6) shows the effect of varying homogenization time on the breakage, emulsion diameter, and VOILELM stability. Initially, the homogenization time was insufficient for proper emulsification. However, at 5 min of homogenization time, a highly stable VOILELM was obtained, with a high stability of 134 min and minimum breakage. However, any further increase in homogenization duration caused the stability to decline, due to the increased transport of water molecules, diluting the internal stripping phase, and resulting in an unstable emulsion, as reflected in larger emulsion diameter and breakage. Moreover, longer homogenization time results in an increased breakage of emulsion owing to high internal shearing, whereby smaller droplets are formed.[43] These droplets possess high interaction capacity and coalesce quickly, giving rise to larger droplets.[44] Similar observations were reported for the extraction of ciprofloxacin ELM.[45] These results are in agreement with a similar study on lactic acid extraction where 20 min of homogenization was adequate at a speed of 2000 rpm.[34]

At these optimized conditions, the diameter of emulsion was measured. Figure 7 shows the emulsion diameter obtained by using DLS for the freshly prepared VOILELM and the VOILELM after exposure to the external LA solution. The microscopic images obtained under the same conditions are presented in Figure S1 (Supporting Information). At these stable conditions, the lactic acid extraction efficiency was 96.08%.

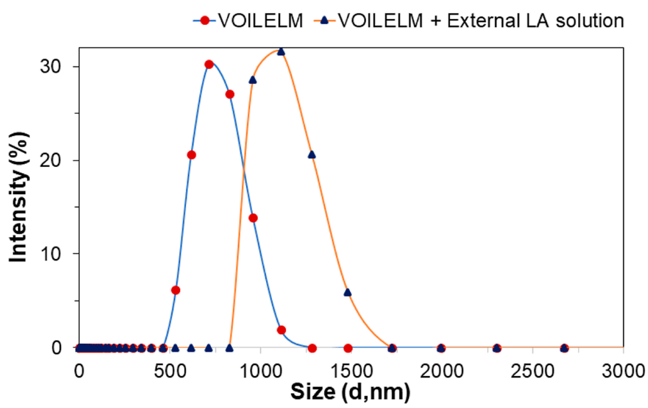

Figure 7. Emulsion droplet size of (a) VOILELM and (b) VOILELM after exposure to an external LA solution. Experimental conditions: SFO: 10 mL, Span 80 concentration: 1 wt %, NaOH concentration: 0.15 M, [TMAm][Ac] concentration: 0.3 wt %, phase ratio: 0.25, homogenization speed: 5200 rpm, homogenization time: 5 min, treat ratio: 3, stirring speed: 270 rpm, stirring time: 20 min, and settling time: 5 min.

2.7. Verification of the Optimized Results.

At the optimized conditions obtained, experiments were performed to validate the efficacy of the VOILELM. The experiments were performed in triplets and the mean values were reported. The results reveal that the optimized conditions are as follows: SFO: 10 mL, Span 80 concentration: 1 wt %, NaOH concentration: 0.15 M, [TMAm][Ac] concentration: 0.3 wt %, homogenization speed: 5200 rpm, homogenization time: 5 min, treat ratio: 3, stirring speed: 270 rpm, stirring time: 20 min, and settling time: 5 min. A highly stable and effective VOILELM with 1.34% minimum breakage, 1.16 μm emulsion diameter, 131 min standalone stability, and 96.08% lactic acid extraction efficiency was observed.

3. CONCLUSIONS

Stability is an important parameter that affects the efficacy of VOILELMs. Carrier incorporation can enhance the stability of VOILELMs by manifold. Due to their greener characteristics compared to conventional solvents, ILs are suitable alternatives as carriers. In this work, a VOILELM was developed using IL-[TMAm][Ac] as the carrier. The stability of the resulting

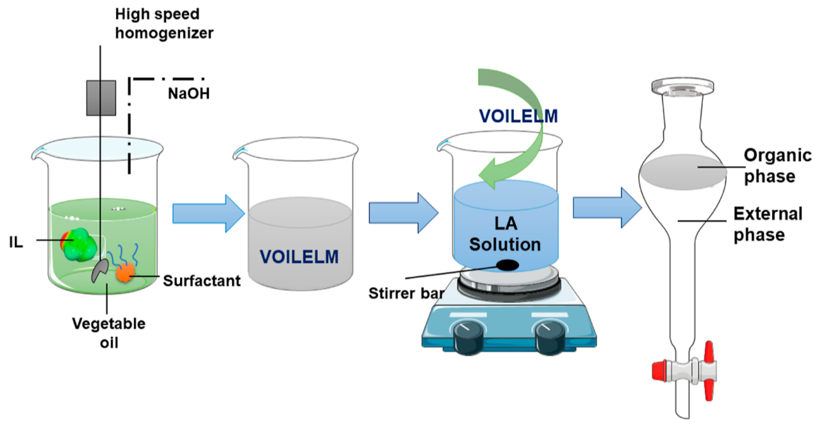

Figure 8. Schematic diagram of the method adopted for LA extraction through VOILELM.

VOILELM was investigated, measuring the breakage (%), standalone stability (min), and emulsion globule diameter (μm). Since the ELM composition and shear affect its stability, the effects of surfactant concentration, internal stripping agent concentration, carrier concentration, phase ratio, homogenization speed, and homogenization time on stability were investigated. The results suggest that 1 wt % Span 80 concentration, 0.15 M NaOH concentration, 0.25 phase ratio, 5200 rpm homogenizer speed, and 5 min homogenization time were the most optimal for producing a highly stable VOILELM. Indeed, under these conditions, the breakage was 1.34%, and the emulsion was highly stable for more than 2 h (132 min) with a minimum globule size of 1.16 μm, while 96.08% extraction efficiency was achieved.

4. EXPERIMENTAL SECTION

4.1. Materials. Lactic acid (LA) (>98%) was purchased from Merck, Germany, while [TMAm][Ac], Span 80, and NaOH were procured from Sigma-Aldrich. Sunflower canola oil was purchased from LOTUS Seri Iskandar. Table S1 presents the basic properties of chemicals employed in this work.

4.2. VOILELM Preparation. In this work, the VOILELM was developed using a method established as a part of our previous study. Briefly, 10 mL of sunflower canola oil was used as a diluent because of its renewable and green nature. Then, 1 wt % of Span 80 and 0.2 wt % of IL [TMAm][Ac] were added to the oil. The resulting mixture was homogenized using an ULTRATURRAX HIGH SPEED T-25 homogenizer, Germany, at 5200 rpm for 3 min, after which 1.25 mL of NaOH was added dropwise, followed by homogenization at 5200 rpm for 5 min, resulting in a milky VOILELM.

The emulsion was mixed with the LA external solution of 0.5 M concentration (treat ratio = 3), followed by stirring at 270 rpm for 20 min. The treat ratio is defined as the ratio of the external phase of the membrane phase. Extraction and stripping were performed in a single step, after which the solution was transferred to the separating funnel, resulting in the formation of two layers. The upper layer consisted of the organic phase, and the lower layer was formed by the external aqueous solution. Figure 8 presents the schematic diagram of the method adopted for the extraction of LA using VOILELM. The lower aqueous phase was filtered using a syringe, after which the concentration was measured using UV−vis at a wavelength of 390 nm. The organic phase was recovered and reused for LA extraction. The extraction efficiency was evaluated using the following equation:

$$\text{Efficiency}(\%) = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

where C_i = the initial concentration of lactic acid in the external phase and C_f = the concentration of lactic acid in the aqueous phase after extraction.

4.3. VOILELM Characterization. pH measurements were performed using a digital pH meter with a pH electrode (ECFC7252101) calibrated at pH values of 4 and 7 for VOILELM, initial external phase, and VOILELM external phase at room temperature. VOILELM viscosity was measured using a Brookfield viscometer CAP 2000 + version 1.5, purchased from Ametek Bhd, Malaysia. Measurements were conducted at 25 °C using spindle 5 for a run time of 60 s at a shear rate of 3000/s. The emulsion globule diameter was measured using dynamic light scattering (DLS). A computerized inspection system (Zetasizer Nano series, Malvern Instruments, United Kingdom) was used. The microscopic images of emulsion were captured using an Eclipse LV 100N Pol microscope equipped with a camera and Toupview software for image analysis. All experiments were performed in triplicate at room temperatures and mean values were reported.

4.4. Stability Analysis. The stability analysis involved the determination of emulsion breakage, emulsion globule size, and standalone stability at different reaction conditions.

4.4.1. Breakage. Emulsion breakage was evaluated using the following equation

$$\in = \frac{V_s}{V_i} \times 100 \tag{2}$$

where V_s = the volume of the internal stripping agent leaked into the external solution, V_i = the initial volume of the internal stripping agent, and V_s was calculated using the equation

$$V_s = V_{ext}\frac{10^{-pH_0} - 10^{-pH}}{10^{-pH} - C^{i}_{OH-}} \tag{3}$$

where V_{ext} = the volume of the external aqueous phase. pH_0 = the initial pH of the external phase. pH = the external phase pH after being dispersed in the emulsion phase. $C_{OH}{}^{i}$ = the initial OH^- concentration in the internal phase.

4.4.2. Standalone Stability. The standalone stability—also referred to as statistical stability—is the time period during

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which the emulsion is stable. It is determined by placing the freshly developed emulsion in a vial. The initial time is recorded, and the emulsion stability is visually observed. The time point at which the aqueous layer starts to appear in the vessel is also noted (indicating that the emulsion is starting to break), allowing the period during which the emulsion is stable to be calculated. Figure 9 shows the standalone stability analysis of VOILELMs.

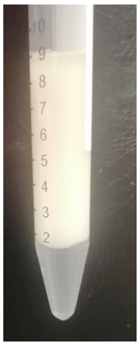

Figure 9. Standalone stability of VOILELMs, depicting the breakage of emulsion and aqueous phase.

4.4.3. Emulsion Globule Diameter. The emulsion diameter provides extensive information on emulsion diameter variations and is thus used to measure the VOILELM stability. The diameter of the freshly manufactured VOILELM was measured before and after it was dispersed in an external LA solution using DLS, and microscopic images were captured using a microscope. A drop of sample was placed on a glass slide, and the images were captured using the microscope. For the freshly synthesized VOILELM to be highly stable, the emulsion diameter must be 0.8−3 μm.[46]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c03425.

> List of chemicals; effect of various parameters on breakage, emulsion diameter, and standalone stability; and microscopic images of VOILELMs (PDF)

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Notes

The authors declare no competing financial interest.

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