Effect of bulk viscosity, emulsion droplet size on the separation efficiency of model mineral oil-in-water (O/W) emulsions under ultrasonic standing wave fields: A theoretical and experimental investigation

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TOC Graphical Abstract:

Abstract:

Ultrasound standing waves can be used to separate emulsions. So far, they have been applied to oil-in-water emulsions with low continuous phase viscosity. There is a potential to use this technique for novel applications such as separating lipids from algal biomass, however this requires the methodology to be optimised to process viscous emulsions. We have addressed this issue by studying the effects of bulk phase viscosity (1 to 23 mPa.s), emulsion droplet size (4.5 to 20 μm), power (10 to 54 W/L) and frequency (1 and 2 MHz) of ultrasound on the separation efficiency of model mineral oil-in-water-glycerol-mixture emulsions. For the small droplet size (4.5 μm) emulsion in water, the maximum separation achieved increased from 36 to 79% when ultrasound power increased from 10 to 54 W/L. However, for the large droplet size (11 μm) emulsion, the maximum separation was greater than 95%, and was independent of ultrasound power. The maximum separation efficiency for small droplet size (4.5-6 μm) emulsions decreased from 80 to 14% when the viscosity increased from 1 to 23 mPa.s. However, for the large droplet size (11-20 μm) emulsion, the maximum separation efficiency decreased from 98 to 62% when the viscosity of the bulk phase was increased from 1 to 23 mPa.s. The experimental results were then interpreted using analytical and numerical simulations by calculating time required for the emulsion droplets to migrate to the nearest

pressure anti-nodal plane under the influence of ultrasound standing waves. Further experiments showed that increasing ultrasound frequency from 1 MHz to 2 MHz increased the maximum separation from 36% to 86% for fine emulsions and water as the continuous phase.

1. Introduction

Phase separation of emulsions is crucial in many industrial applications such as fat separation from milk¹⁻⁵, extraction of vegetable and palm oil⁶⁻⁹ and water separation from crude oil¹⁰⁻¹⁹. Ultrasonic standing waves have been effective at separating emulsions in which the continuous phase viscosity is similar to that of water. For example, fat separation from milk using an ultrasonic standing wave field is well-established^{1-5, 20}. Juliano et al. have shown that creaming of milk fat globules can be accelerated using ultrasonic standing wave fields of 400 kHz or 1.6 MHz through the promotion of flocculation and coalescence of the emulsion droplets¹. Juliano et al. have also tested various combinations of single and multiple frequencies and demonstrated effective milk fat separation up to litre-scale systems². While standing wave separation has been established for emulsions with a low-viscosity continuous phase²¹, the effect of increased bulk phase viscosity is not well explored²². Recently, Luo et al.¹⁸⁻¹⁹ showed that it is possible to separate model water-in-oil petroleum emulsions with a continuous phase viscosity 1400-times greater than water using low-frequency (20-40 kHz), high-intensity standing waves. The use of high-frequency (>1 MHz) low-intensity ultrasound may offer advantages for highly viscous systems with industrial applications such as emulsion separation from viscous biological suspensions consisting of ruptured microalgae slurries generated during solvent extraction of lipids²³⁻²⁷. High-frequency low-intensity ultrasound is mild and does not produce acoustic cavitation that might degrade valuable biological compounds to be extracted. Currently there is a lack of understanding of how the viscosity of the bulk phase affects the separation of O/W emulsions using high-frequency low-intensity ultrasound. There is a need to systematically investigate the effects of bulk phase viscosity, emulsion droplet size, and ultrasound frequency and power on the separation efficiency of viscous O/W emulsions.

Although there has been much experimental investigation of emulsion separation using ultrasonic standing wave fields, there is no universal model currently available that can be used to directly compare experimentally observed separation efficiencies to theoretical predictions. The physics of emulsion separation ultrasonic standing wave is complex. When an emulsion is subjected to ultrasonic field with a reflector such as air-water/oil-water interface or metal plate, the superposition of transmitted and reflected sound waves results in the formation of a standing wave field with pressure nodes and anti-nodes (Figure 1)^{10, 28-35}. The difference in the density and compressibility between the droplets and the bulk phase causes an acoustophoretic effect in which the dispersed droplets to migrate either to nodes or antinodes in the fluid via a so-called primary radiation force. Once they reach the nodal planes, a secondary force (Bjerknes force)³⁶⁻³⁷ acts between the droplets to promote coalescence or coagulation of the droplets. The resulting increase in the size of the

droplets/flocs increases their buoyancy accelerating droplet creaming and subsequent phase separation of the emulsion. These processes take place sequentially and simultaneously. For example, during the first few seconds/minutes of sonication, depending on the viscosity of the bulk phase, the emulsion droplets migrate towards the closest pressure anti-nodes (i.e. for oil droplets which are less dense than a continuous aqueous phase). As they encounter neighbouring emulsion droplets, they collide, possibly coalesce and rise faster due to increased buoyancy towards the anti-nodal plane. Detailed kinetic modelling needs to consider the stochastic nature of the random collisions and coalescence events of the migrating droplets.

Figure 1. Schematic representation of the effects of ultrasonic standing waves on emulsion droplets. (a) Forces acting on and between the dispersed emulsion droplets in a standing wave field. (b) Illustration of the migration path of a single droplet in response to the ultrasonic standing wave field. (c) Representation of an ultrasound field imposed on an emulsion, showing pressure nodes and antinodes, including an optical image from our experiments.

In addition, the time and length scales involved in the process vary by a few orders of magnitude. The oscillation time scales for MHz frequencies are on the order of few microseconds, whereas the time needed for the emulsion droplets to migrate to the nodes and antinodes is in the order of a few seconds to minutes, depending on the droplet size and bulk phase viscosity. Experimentally observable phase separation from creaming, may occur over many minutes. The length scales involved in the separation also vary considerably. Emulsion droplets are generally in the order of microns, whereas the wavelengths of MHz frequency ultrasonic (US) standing waves are in the order of few millimetres. The separation vessel geometries are generally in the order of centimetres to meters. Such variation in both time and length scales makes it difficult to develop a universal model to predict the experimentally observed separation efficiencies.

Nevertheless, there was a recent attempt to employ Lattice Boltzmann (LB) numerical simulations by Wang et al.³⁸ to capture the complexity of the formation of standing waves in an oil-in-water emulsion system. The simulations predicted that increasing the US frequency would improve the separation efficiency. However, due to the complexity of the model the simulations were run for <1 millisecond, meaning that the qualitative predictions of increased separation relied on the use of a structure factor. To directly compare with experiments, simulations need to be run for seconds or minutes. Relatedly, Trujillo et al.³⁹ used multiphysics simulations to model the formation of standing waves and the separation of solid particles from liquid. However, the simulations were only carried out for a specific set of experiments and not for generalised separation conditions. The mass fraction of emulsions before and after ultrasonication were compared and matched to the experimentally observed values. However, the predictive simulations as a function of emulsion droplet size, continuous phase viscosity, and the power and frequency of ultrasound were not explored.

In view of the limitations of existing experimental and numerical studies involving US standing waves, there is a need for a simplified theoretical approach. In this study, the complexity of US standing wave separation was deconstructed into a few simple steps. First, the time needed for the migration of a single emulsion droplet under the influence of the primary acoustic radiation force from a pressure node to the closest pressure anti-node was calculated for various droplet sizes and viscosities of the bulk phase as a function of ultrasonic power. Then, the time needed for the coalescence of two emulsion droplets separated by a known distance under the influence of the secondary force was calculated for various drop sizes and viscosities of the bulk phase as a function of power. While the times scales involved are valid only for a few non-interacting emulsion droplets suspended in a bulk continuous phase, they can indicate qualitatively how the separation rate will be affected by the parameters of interest. However, real emulsions contain multiple droplets. In order to capture the standing wave formation in presence of multiple droplets of equal size, COMSOL® multiphysics (pressure acoustics combined with particles in fluid flow) simulations were carried out to investigate the effect of continuous phase viscosity, emulsion droplet size and frequency of ultrasound on the band formation times scales.

In this study, a systematic experimental and theoretical approach is developed to investigate the effects of bulk phase viscosity, the emulsion droplet size, frequency and power of ultrasound on the separation efficiency of O/W emulsions under the influence of high-frequency low-intensity ultrasound.

2. Materials and Methods

2.1 Emulsion preparation

Emulsions were prepared using mineral oil (Sigma Aldrich, USA) as the dispersed phase, Milli-Q water (Millipore, Milli-Q academic) and glycerol (Australia Univar analytical reagent Co., Ltd.) mixtures as the continuous phase, and Tween-20 (Sigma Aldrich, USA) as the surfactant, added to the continuous phase at 0.005% (w/w). The viscosity of continuous phase

was changed by adding different concentrations of glycerol to water. The mass fraction of emulsion droplets was 5% in all experiments. The physical parameters of the continuous and dispersed phases are shown in Table S1.

Water-glycerol mixtures containing 0.005%(w/w) Tween-20 and mineral oil were mixed in a beaker to a total volume of either 133 mL or 266 mL (Table S2) and blended using an Ultra-Turrax (IKA-WERKE, T25 Basic) at 13,500 RPM for various times (Table S2). Selected emulsions were then sonicated for different time intervals (10 to 30 minutes) using an 11 mm tip horn sonicator (Branson digital sonifier, 102C CE horn model) operating at 20kHz with a power input in the range of 14.6 to 34 W to obtain required emulsion drop sizes. The detailed emulsification parameters are shown in Table S2. The disperser homogenizer position was set in a fixed location and ice bath was used to avoid the heating of the emulsions during preparation.

Prior to measurement of the droplet size, the emulsions prepared using only the UltraTurrax were degassed for 6 minutes in a desiccator connected to in house vacuum line, in order to remove any entrained air bubbles. The droplet size distribution was measured using a laser diffraction particle size analyser (Malvern Mastersizer 3000) within 5 minutes after the emulsions were made to avoid effects of droplet coalescence. For the measurement, a few drops of fresh emulsion were dripped into the instrument's measuring beaker (Malvern Hydro EV) and the particle size distribution determined by the instrument using Mie scattering theory. Each sample was measured at least 5 times and the droplet size expressed as the volume moment mean (De Brouckere Mean Diameter), denoted as $D[4,3]$ from at least 3 independent emulsions samples.

2.2 Emulsion separation

For each emulsion separation experiment, a freshly prepared emulsion (~133 mL) was gently loaded into a rectangular ultrasonication chamber fitted with a plate type transducer (50 mm diameter, Honda) operating either at 1 or 2 MHz (Figure 2). In the cases where 266 mL of emulsion was prepared, it was split into two 133 mL batches, one of which was used for the US standing wave separation experiment and the other used for a control experiment with no ultrasound applied. The dimensions of the vessel used in the control experiments matched that of US standing wave separation vessel. 1 mL of emulsion was sampled from a fixed position of the bulk of emulsion using a 1 mL pipette. This emulsion was used to calculate the initial amount of the dispersed phase present in the emulsion and marked as $t = 0$. This reference amount was used to calculate how much of the dispersed phase was separated from the bulk phase and is referred to as the % mineral oil separated from bulk. The emulsion was then subjected to an ultrasonic standing wave field at various nominal powers of 1, 5 or 10 W. Calorimetric calibration determined the actual power delivered to the samples was 1.3, 3.3 or 7.2 W, respectively when operating at 1 MHz. This translated to a specific power of 10, 25 and 54 W/L, respectively. In the case of 2 MHz sonication, the actual delivered power was 1.6 or 4.5 W for 1 and 10 W of nominal power, respectively, corresponding to specific powers

of 12 and 34 W/L. After 2 minutes of ultrasound irradiation, the standing wave field was switched off and 1 mL of emulsion was pipetted from a fixed position (35 mm from top) of the emulsion and transferred to glass vial with a liquid tight lid. After a stoppage for 1 minute, the ultrasound standing wave field was recommenced for another 2 minutes. This procedure was repeated until the final irradiation time of either 12 or 14 minutes was reached. For each experiment, a control emulsion separation experiment was carried out without applying any ultrasonication, in which the emulsion separation occurred as a result of the native buoyancy of the droplets.

Figure 2. (a) Schematic of ultrasonic separation chamber applied to separate mineral oil from oil-in-water emulsions. (B) Standing wave formation at 1 MHz as visualised using chemiluminescence⁴⁰. The standing wave pattern shown here is obtained in our lab using Luminol (c) Optical image of the ultrasonic chamber showing oil phase-separated from the emulsion after being subjected to the standing wave field.

The amount of mineral oil in the 1 mL samples of emulsion taken after various ultrasonication times, was determined gravimetrically using a solvent extraction method. This involved addition of 1 mL of ethanol to destabilise the emulsion followed by addition of 5 mL of hexane to extract the mineral oil from the sample. After tumbling and rotating the glass vial for 2 hrs, the vials were centrifuged at 1331 g for 10 minutes (Beckman Coulter X-30R centrifuge, Beckman 10E 78 serial rotor) to separate the hexane containing the dissolved mineral oil from the water phase. After centrifugation, there was a top layer consisting of a hexane-mineral oil mixture and a bottom aqueous layer. The bottom aqueous layer was gently removed, and the remaining hexane-mineral layer was gently transferred to a glass vial of known weight. The hexane-mineral oil mixtures were dried under a stream of nitrogen at 60 °C using a Techne Sample Concentrator (model DB-3D Dri-Block, Bibby Scientific Limited, Stone, UK) to remove the solvent. The mass of the remaining mineral oil was then measured.

Standing wave formation at 1 MHz was visualised using chemiluminescence measurements, where the bulk water phase contained 0.1 mM luminol (Sigma Aldrich) and 0.1 M NaOH ⁴⁰. Chemiluminescence occurs when OH radicals, generated during acoustic cavitation react with luminol molecules. Long exposure digital image recording was carried out in order to capture the standing wave field. Note that chemiluminescence experiments were carried out at relatively higher power levels (under cavitation conditions) for the visual observation of the standing waves. The de-emulsification experiments were carried out under non-cavitating conditions, as mentioned earlier.

2.3 Theoretical modelling and numerical simulations

Emulsion separation by ultrasound standing waves can be qualitatively analysed through theoretical modelling. When doing so, the whole process is simplified by deconstructing the complexity into a few simple steps (Figure 1). First, the time needed for migration of a single emulsion droplet from a pressure node to the closest pressure anti-node ($\sim \lambda/8$) was calculated under the influence of the primary acoustic radiation force. The time was calculated for various droplet sizes and viscosities of the bulk phase (Table S1) as a function of ultrasound power. Then the time needed for the coalescence of two emulsion droplets separated by a known distance under the influence of secondary acoustic forces was calculated for various droplet sizes and bulk phase viscosities as a function of ultrasound power. These time scales qualitatively indicate how separation will be affected by the parameters of interest.

The dynamics of a single emulsion droplet suspended in a bulk phase are represented schematically in Figure 1. Since the pressure of an ultrasound standing wave oscillates very rapidly relative to the bulk movement of the emulsion droplet, the movement of the emulsion droplet cannot be determined over an individual period of oscillation but rather as an overall or time-averaged effect over multiple oscillation phases occurring during a period of exposure to an ultrasound standing wave. The time-average primary acoustic radiation force acting on a droplet is given by ^{32-33, 36, 41-45},

$$F_{1,ac} = 4\pi r^3 E_{ac} K_s(\tilde{\rho}, \sigma) \sin(2kz) \quad (1)$$

where r is the radius of the droplet, $k = 2\pi/\lambda$ is the wavenumber, and λ is the wavelength of the standing wave that is the ratio of the speed of sound in the medium to the ultrasound frequency ($\lambda = c_o/\nu_o$). E_{ac} is the time-average energy density that is dependent on the intensity of the acoustic wave I . $K_s(\tilde{\rho}, \sigma)$ is the acoustophoretic coefficient, $\tilde{\rho}$ is the density ratio of the droplet (ρ_d) and the continuous phase (ρ_o), and σ is the ratio of the speed of sound ratio in the droplet medium (c_d) and the continuous phase (c_o). The definitions of E_{ac} and $K_s(\tilde{\rho}, \sigma)$ are, respectively,

$$E_{ac} = \frac{P_o^2}{4\rho_o c_o^2} \quad (2)$$

$$K_s(\tilde{\rho}, \sigma) = \frac{1}{3} \left[\frac{5\tilde{\rho} - 2}{2\tilde{\rho} + 1} - \frac{1}{\tilde{\rho}\sigma^2} \right] \quad (3)$$

in which P_o is the acoustic pressure amplitude. To obtain P_o , we firstly consider the relation between the energy density E_{ac} and the intensity of acoustic wave I , which is

$$I = 2E_{ac}c_o \quad (4)$$

The intensity I can be estimated based on the input power of the mechanical vibration W and the size of the transducer as

$$I = \frac{W}{A_{\text{transducer}}} = \frac{W}{\pi R_{\text{transducer}}^2} \text{ hence } P_o = \sqrt{\frac{2\rho_o c_o W}{\pi R_{\text{transducer}}^2}} \quad (5)$$

where $R_{\text{transducer}}$ is the radius of the transducer. In our experimental setup, $R_{\text{transducer}} = 25$ mm.

Under the assumptions that the inertial force is negligible and that the droplet moves in a quasi-steady state at a velocity $v_1(z)$, the primary acoustic force, buoyancy and the Stokes flow drag are in balance as:

$$F_{1,ac} + F_g + F_{1,\mu} = 0 \quad (6)$$

where

$$F_{1,\mu} = 4\pi \left(\frac{1 + \frac{3\tilde{\mu}}{2}}{1 + \tilde{\mu}} \right) \mu_o r v_1(z), \quad (7)$$

$$F_g = \frac{4}{3} \pi (\rho_d - \rho_o) r^3 g. \quad (8)$$

$g = 9.81$ m/s is the acceleration due to gravity, and $\tilde{\mu}$ is the density ratio of the droplet (μ_d) and the continuous phase (μ_o).

As the droplet is assumed to move in a quasi-steady state, introducing the three expressions of the primary acoustic force (1), buoyancy (7) and the Stokes drag (8) into the force balance equation (6), the moving velocity $v_1(z)$ of the droplet along the direction of the wave propagation can be obtained. Then, by using a simple Euler time advancing scheme, the moving distance Δz of the droplet due to the acoustic force during a short time-step Δt can be calculated by $\Delta z = v_1(z)\Delta t$. Adding all these distance segments up over time, we obtain the distance that the droplet moves. In the same manner, if we know the distance of the droplet movement, we can get the time required for that movement of a single droplet over that distance in a standing wave under various conditions, such as power input and continuous phase viscosity. In all of our calculations, we used $\Delta t = 1$ μ s. Though this time frame is about 1000 times that of the standing wave period, it is less than 0.0001 of the time needed for a droplet to move the distance of $\lambda/8$ in our system.

To investigate the interactions between droplets, two emulsion droplets, which are congregated at the pressure anti-nodal plane and are separated by a distance, h are considered. The secondary force (Bjerknes force) between two droplets^{32, 36-37, 43} can be expressed as

$$F_{2,ac} = 4\pi r^6 \left[\frac{(\rho_d - \rho_o)(3 \cos^2 \theta - 1)}{6\rho_o h^4} v_2^2(z) - \frac{\omega_o^2 \rho_o (\beta_d - \beta_o)^2}{9h^2} p^2(z) \right] \quad (9)$$

where $v_o = \omega_o/2\pi$ is the frequency of US, θ is the angle between the centreline and the direction of wave propagation, $\beta_d = 1/(\rho_d c_d^2)$ and $\beta_o = 1/\rho_o c_o^2$ are the compressibility of the droplet and water correspondingly. Under the assumption that the inertial force is negligible, and the droplet moves in a quasi-steady state with velocity $v_2(z)$, the balance of the secondary acoustic force and the Stokes flow drag is shown as:

$$F_{2,ac} + F_{2,\mu} = 0 \quad (10)$$

where

$$F_{2,\mu} = 4\pi \left(\frac{1 + \frac{3\tilde{\mu}}{2}}{1 + \tilde{\mu}} \right) \mu_o r v_2(z) \quad (11)$$

Introducing the two expressions of the secondary acoustic force equation (9) and the Stokes drag with respect of $v_2(z)$ in equation (11) into the force balance equation (10), the moving velocity $v_2(z)$ due to the secondary acoustic force can be calculated. Following the same idea to determine the migration time, the time required for one droplet to meet the adjacent droplet in the emulsion so they coalesce can be calculated. It is worth noting that in our calculations, we focus on the coalescing time at the band. As such, we let $\theta = 0$. Also, details of the choice of h can be found in Section S1.3 of Supplementary Information.

Though the theoretical modelling based on an analysis of forces on one or two droplets can help improve our understanding of emulsion separation by ultrasound waves, real emulsions contain multiple droplets. In order to capture the standing wave formation in presence of multiple droplets, COMSOL® multiphysics simulations were made of multiple emulsion droplets in standing wave fields. Simulations were carried in two steps. First, the pressure acoustics model equation (Equation S1) was solved in the frequency domain at a fixed frequency of 1 MHz and a domain length and width of 2λ and 3λ , respectively. The acoustic pressure intensity calculated from the power and transducer area was used as a boundary condition for the ultrasound source. The steady state pressure distribution thus obtained showed the formation of standing waves with low- and high-pressure regions. Details of the pressure distributions are shown in Supplementary Information (Figure S1). Once a steady state pressure was achieved, the domain was then seeded with 10,000 emulsion droplets of known size and properties such as density, speed of sound and bulk modulus. The properties of a mineral oil emulsion were used as shown in Table S1. Unsteady particle fluid flow

simulations were then carried out in sequence by inputting the steady state pressure distribution from the pressure acoustics model. The particle fluid flow model takes acoustophoretic force, gravity and viscous drag into effect, similar to the analytical method used here to calculate droplet migration times.

3. Results and discussion

3.1 Effect of droplet size and US power and frequency on emulsion separation

The percentage of mineral oil separated from the bulk (water) as a function of sonication time at 1 MHz is shown in Figure 3. As the concentration of surfactant (Tween-20) used to make the emulsion was very low (0.005 wt%), the emulsions can be considered as metastable. During sonication the emulsion droplets congregate at the pressure nodal planes due to primary radiation force, coalesce due to secondary forces, and separate into a clear upper phase as shown in Figure 2 (c). The separation kinetics for control experiments performed in the absence of an US standing wave field are also shown for comparison. In the case of the emulsion with droplets of 11 μm , the maximum separation achieved in the control experiment by buoyancy was only 14%. In contrast, when subjected to an ultrasonic standing wave field, near-complete separation (>95%) was achieved within 4 minutes at 0.025 and 0.054 W/mL, and within 8 minutes at a lower power density of 10 W/L. There was no improvement in separation with further sonication. An increase in power from 1 to 5 W halved the time for required maximum separation, but a further increase in power to 10 W did not improve the separation. For the smaller droplet size (4.5 μm), the maximum separation achieved by buoyancy alone was only 8%, compared to 36%, 63% and 79% within 12 minutes of sonication at 10, 25 and 54 W/L, respectively. It is interesting to note that the separation did not saturate within the experimental sonication time of 12 minutes, indicating further sonication could have potentially resulted in more complete separation of the emulsion.

Figure 3. The effect of emulsion droplet size and ultrasound power on the separation of mineral oil from mineral oil-in-pure water emulsions at ultrasound frequency of 1 MHz. The average diameter ($D[4,3]$) of the emulsion droplets were 4.5 and 11 μm . As a control, the separation (by buoyancy) of emulsions without ultrasound is also shown (circles). Open symbols correspond to 4.5 μm and closed symbols correspond to 11 μm drop size emulsions. The stated nominal powers of 1, 5 and 10 W correspond to actual delivered powers of 1.3, 3.3 and 7.2 W respectively. The volume of emulsion used in the experiment is 133 mL, hence the specific powers are 10, 25 and 54 W/L, respectively.

These results can be rationalised from theoretically calculated single droplet migration times as presented in Figure 4. As explained above, the migration times were calculated based on the influence of the primary acoustic radiation force only. The results show that the time required for the migration of a droplet to an antinode decreases with an increase in ultrasound power density and frequency (for a given bulk phase viscosity and emulsion droplet size) (Figure 4).

Figure 4. Predicted ultrasonic standing wave emulsion droplet kinetics as function of droplet size, ultrasonic power density and frequency with water as the continuous phase. The data are theoretically calculated times required for i) a single mineral oil emulsion droplet to reach the pressure anti-nodal plane ('time to node') and for ii) coalescence of two adjacent mineral oil emulsion droplets due to secondary forces (Bjerknes force) when subjected to ultrasound standing wave fields at 1 and 2 MHz frequencies. Droplets with a diameter of 4.5 μm or 11 μm are assumed to start $\lambda/8$ away from the node. The effect of primary acoustic radiation force acting in the direction of propagation of sound wave is considered for the time to node

calculations. Zero ultrasound power density corresponds to the case where there is no ultrasound applied, hence the time required for the drop to rise $\lambda/8$ under the influence of only buoyancy force is presented as the 'time to node'.

The predicted migration times ('time to node') for an 11 μm droplet in water were about 15, 10 and 8 seconds for ultrasound power densities of 10, 25 and 54 W/L, respectively. The power of the standing wave ultrasound was predicted to have a similar effect on the relative migration times of the smaller, 4.5 μm emulsion droplets, which were about 87, 62 and 50 seconds, respectively for 10, 25 and 54 W/L. Such a significant effect of ultrasound power and droplet size on the migration time of the droplets to the nodes (Figure 4), can help to the observed effects of power and droplet size on the separation efficiency (Figure 3).

COMSOL® multiphysics simulations of multiple emulsion droplets in water subjected to 1 MHz US standing wave fields at 54 W/L are shown in Figure 5. As time progresses, the sparsely distributed emulsion droplets are predicted to aggregate at pressure antinodes (Figure 5b) resulting in the formation of bands similar to those observed in the experiments (inset of Figure 1a). The wavelength of band formation from the COMSOL simulations matched with the experiments, providing some validation of the pressure acoustic model. As shown in Figure 5b, bands were formed within 7 s and 41 s for droplets of 11 μm and 4.5 μm , respectively. These times are comparable to the droplet migration times of 8 seconds and 40 s calculated from analytical theory (Figure 4).

Figure 5. Outputs from COMSOL® multiphysics simulations (pressure acoustics combined with emulsion droplets in fluid flow) of the emulsion droplets in water subjected to 1 MHz US standing wave fields at 54 W/L. The emulsion droplets are coloured by velocity in $\mu\text{m/s}$. The scale bar for velocity is shown on the right. (a) Initial uniformly dispersed emulsion drops. (b) Distribution of 11 μm sized emulsion droplets after 7 s of 1 MHz US. (c) Distribution of 4.5 μm sized emulsion droplets after 7 s of 1 MHz US. (d) Distribution of 4.5 μm sized emulsion droplets after 41 s of 1 MHz US. The band formation time was determined based on the point at which no further decreases in band thickness could be observed.

Separation of emulsions using US standing waves depends on both the migration of droplets to the pressure antinodes and subsequent coalescence of the congregated droplets. Coalescence is promoted by the secondary force (Bjerknes force) acting between the droplets, which is very small compared to the primary radiation force that causes the droplets migrate to the antinode. According to the analytical calculations it was predicted that, under the influence of the secondary force, the time required for a droplet to find another adjacent droplet in the sparse emulsion system (5% mass fraction) was in the order of hours (Figure S4, Supplementary Information). However, for droplets that have migrated to the nodal plane (inset Figure 1c), the distance between two adjacent droplets is significantly decreased. As it is very difficult to experimentally determine the distance between congregated droplets, this distance was assumed to be about 1/100 times the initial distance between the drops ($h =$

$l/100$). Based on this, coalescence times for the droplets at a pressure anti-nodal plane that are separated by a distance ' h ' were calculated for emulsions containing droplets of 4.5 μm and 11 μm in water (Figure 4).

For a given bulk phase viscosity and emulsion droplet size, the coalescence time was predicted to decrease with an increase in the power density of ultrasound (Figure 4). While the predicted coalescence times were lower than the predicted droplet migration times, the effect of ultrasound power was relatively greater on coalescence than migration times. The coalescence times were predicted to decrease approximately 10-fold with an increase in ultrasound power density from 10 to 54 W/L. At lower powers, the predicted coalescence times were reasonably close to migration times, whereas at higher powers they become much shorter than the predicted migration times. This suggests that the considerable improvement in separation kinetics observed between 10 to 25 W/L (Figure 3) could be due more to improved coalescence than reduced migration time.

The coalescence times were much shorter for the larger droplets (11 μm) than the smaller droplets (4.5 μm) (Figure 4). This may help to explain why the maximum separation efficiency of the emulsion with 11 μm droplets did not depend on the power (Figure 3). The observations that the separation of emulsions with smaller droplets is more significantly affected by power than coarser emulsions is in agreement with experimental studies carried out by Juliano et al.¹ on milk systems.

In order to simulate the physics occurring during separation more accurately, the model could be further developed to include the droplet size distribution information obtained by light scattering as an input to the model, rather than the average droplet size used in the current study. The model could also be developed to take into the account binary and multiple random collisions between the droplets migrating to the pressure antinode, and the kinetics of coalescence events occurring during migration and at the antinode. The development of such a model will be carried out by the authors in the future to be able to more accurately compare the simulation results to the experiments.

3.2 Effect of ultrasound frequency on separation

Increase in frequency of ultrasound is expected to improve the separation of emulsions by decreasing the distance between the nodes in the standing wave field. The more pressure antinodes per unit length of the processing vessel, the less time is needed for migration of emulsion droplets to the pressure antinodes. Consistent with this, the migration time of droplets was predicted using our theoretical calculations to decrease by slightly more than a factor of two with an increase in frequency of US from 1 MHz to 2 MHz (Figure 4). Even though in this circumstance, the wavelength of the ultrasound wave is only halved, the sinusoidal behaviour of the primary acoustic force becomes steeper as the wave number (frequency) increases. As such, the migration time for 2 MHz is reduced more than 2-fold relative to that for 1 MHz. To test the effect of frequency experimentally, US standing wave emulsion separation was compared at 1 and 2 MHz using 1 W of US with an average emulsion droplet

size of 4.5 μm and water as the bulk phase (Figure 6). The separation performance was much higher at 2 MHz than 1 MHz, with over 50% recovery achieved in 2 min at 2 MHz, compared to less than 40% recovered after 12 min at 1 MHz. The improvement in separation efficiency at the higher frequency is seemingly more than would be predicted by the decrease in droplet migration time. This could be at least partly explained by the more dramatic reduction in the predicted time to coalesce (of around 5-fold) resulting from the increase in frequency (Figure 4). One key reason for the time of coalescence between droplets being more strongly dependent on the ultrasound frequency than the migration time is that the secondary force is a function of the square of the angular frequency as shown in equation (7).

Figure 6. The effect of ultrasound frequency on the separation of mineral oil from mineral oil-in-pure water emulsion at an ultrasound power of 1 W and for an average emulsion droplet size of 4.5 μm . In the case of 1 and 2 MHz sonication for 1 W nominal power, the actual delivered power was 1.3 and 1.6 W respectively. The volume of emulsion used in the experiment was 133 mL hence the specific powers are 10 and 12 W/L respectively. The 1 MHz and no US data are the same as those shown in Figure 3.

COMSOL multiphysics simulations illustrate the effect of an increase in US frequency on the separation of emulsion droplets (Figure 7). The simulations of an emulsion system with a droplet size of 4.5 μm at low power (10 W/mL) show that the band formation is not complete even at 200 seconds of US application at 1 MHz frequency whereas at 2 MHz the band formation is complete within 50 seconds.

Figure 7. Output of a COMSOL® multiphysics simulation of emulsion droplets in water subjected to 1 and 2 MHz US standing wave field at a power (1W) density of 10 W/L. The emulsion droplets are coloured by velocity in $\mu\text{m/s}$. The scale bar for velocity is shown on the right. (a) Initial uniformly dispersed emulsion drops. (b) The distribution of 4.5 μm sized emulsion droplets after 200 s of 1 MHz US. (c) The distribution after 50 s of 2 MHz US. The band formation time decreased with an increase in frequency from 1 to 2 MHz in accordance with the analytical calculations.

3.3 Effect of continuous phase viscosity on US standing wave emulsion separation

Figure 8 (a) shows the amount of mineral oil separated from an emulsion with a continuous aqueous phase consisting of a 59% glycerol-water mixture as a function of sonication time at 1 MHz. The viscosity of 59% glycerol is 10 mPa.s, which is about 10 times that of water (Table S1). The increased viscosity resulted in a very low separation efficiency of 2.6% in the control sample. When an US standing wave field was present, there was a significant improvement in the separation efficiency. For the emulsion with smaller droplets

(6 μm), the separation efficiency improved with increasing US power. However, the separation efficiency of the emulsion with larger droplets (20 μm) did not depend much on the power (Figure 8(a)). The diminished influence of US power on larger droplets was also seen in the experiments with water as the bulk phase (Figure 3). These results indicate that low-power standing wave ultrasound can be effective in viscous systems if the emulsion droplets are sufficiently large.

Figure 8. The effect of emulsion droplet size and ultrasound power on the separation of mineral oil-in-glycerol emulsions at an ultrasound frequency of 1 MHz. The continuous phase was a glycerol and water mixture with (a) 59% and (b) 70% glycerol, with viscosities 10 and 23 mPa.s, respectively. The average diameters of the emulsion droplets were 6 and 20 μm . Open symbols correspond to small drop size (6 and 6.4 μm) and closed symbols correspond to large drop size (20 μm). Separation in the control experiments that rely on buoyancy alone with no ultrasound applied was negligible for both 6 and 20 μm in 59% and 70% glycerol solutions.

For a given droplet size, the calculated migration time increases with an increase in viscosity as expected (Figure 9). For a given viscosity, the migration time decreases with an increase in droplet size. In comparison, the coalescence times due to the secondary acoustic force were calculated to be weakly dependent on the viscosity for large droplets (Figure 9 (a)) and more strongly dependent on the viscosity at low power for small droplets (Figure 9 (b)). The calculations show that power significantly affects the coalescence times, with the viscosity dependence become almost negligible beyond an ultrasound energy density of 1.7 J/m³ (10 W) for both large and small droplet emulsions.

The experimentally observed differences in the separation of large and small droplet emulsions can also be explained from COMSOL® simulations results shown in Figure S2 (supplementary information). For emulsion droplets of 20 μm dispersed in a 59% glycerol solution, band formation was predicted to occur within 13 seconds, whereas for smaller droplets of 4.5 μm , band formation took almost 150 seconds.

Figure 9. The time required for migration to node (TN) and coalescence (TC) of two adjacent mineral oil emulsion droplets due to primary radiation and secondary Bjerknes force when subjected to an ultrasound standing wave field. Predictions for droplets of $20 \mu\text{m}$ at 1 MHz (a) and 2 MHz (c) US, and for droplets of $6 \mu\text{m}$ at 1 MHz (b) and 2 MHz (d) US. The continuous phase was a glycerol and water mixture with (a) 59% and (b) 70% glycerol, with viscosities 10 and 23 mPa.s, respectively. It is assumed that two adjacent droplets congregated at the pressure anti-nodal plane are separated by a distance of $h = l/100$, where l is the initial distance between the droplets in the absence of the ultrasound field. Zero ultrasound power density corresponds to the case where there is no ultrasound applied, hence the time required for the drop to rise $\lambda/8$ under the influence of only buoyancy force is presented as the ‘time to node’.

Figure 8 (b) presents emulsion separation data as a function of sonication time at 1 MHz with a continuous phase of 70% glycerol, with a viscosity of 23 mPa.s which is about 23 times that of water (Table S1). As with 59% glycerol, the increased viscosity resulted in a very low separation efficiency in the control experiment performed without ultrasound, for both small ($6.4 \mu\text{m}$) and large droplet ($20 \mu\text{m}$) emulsions. Separation efficiency increased with increasing ultrasound power density for the emulsion with $20 \mu\text{m}$ droplets, consistent with a reduction in the calculated droplet migration times as a function of power (Figure 9 (a)). However, applying standing wave ultrasound did not considerably improve the separation of small droplets ($6.4 \mu\text{m}$) regardless of ultrasound, despite a predicted decrease in drop migration

times with increasing power density. The predicted migration times were more than 10 times longer than for the 20 μm droplets (Figure 9 (a) and (b)).

COMSOL simulation results shown Figure S3 (supplementary information) can help explain the experimentally observed differences in the separation of large and small droplet emulsions in 70% glycerol. As observed, for emulsions with droplets of 20 μm dispersed in a 70% glycerol solution, band formation was predicted within 0.5 minutes, almost 5 minutes was required to form a distinct band with 6 μm droplets. These band formation times scales are comparable to analytical calculations, which were around 0.5 and 5.6 minutes for 20 and 6 μm droplets, respectively.

US frequency had no discernible effect on the separation of emulsions in the case of the 59% glycerol bulk phase regardless of droplet size or power density. Even though an increased frequency is supposed to improve the separation (Figure 10), the effect of increased viscosity could have overwhelmed the influence of frequency. In order to test this hypothesis, the ultrasound attenuation coefficient was calculated for water-glycerol mixtures at 1 and 2 MHz using the following equation ⁴⁶

$$\alpha = \frac{2\mu_o(2\pi\nu_o)^2}{3\rho_o c_o^3} \quad (12)$$

where α is the ultrasound attenuation coefficient, μ_o is the viscosity and ρ_o is the density of the medium, ν_o is the frequency of ultrasound and c_o is the speed of sound in the medium. For a given viscosity, the absorption coefficient increases with the square of frequency. Hence the attenuation coefficients for 2 MHz US as shown in Table 1 are approximately 4 times that of 1 MHz US.

Figure 10. The effect of ultrasound frequency on the separation of mineral oil-in-59% glycerol emulsions at ultrasound power densities of 10 and 54 W/L and emulsion droplet sizes of 6-7.5 μm and 20-24 μm . Open symbols correspond to 1 MHz and closed symbols correspond to 2 MHz frequency.

Table 1. Ultrasound attenuation coefficients in continuous and dispersed phases of the emulsions investigated in this study.

Phase	Viscosity (mPa.s)	Attenuation Coefficient (α), 1 MHz	Attenuation Coefficient (α), 2 MHz
Water	1	0.008	0.032
59% Glycerol (wt %)	10	0.050	0.203
70% Glycerol (wt %)	23	0.113	0.453
Mineral oil	27.5	0.358	1.435

The intensity of ultrasound also decreases as a function of distance from the transducer according to the following equation:

$$I = I_0 e^{-2\alpha x} \quad (13)$$

where I_0 is the intensity at the source, α is the ultrasound attenuation coefficient, x is the distance from the transducer. The normalised US intensity is plotted in Figure 11, as a function of distance (x) from the transducer in a sonication chamber of length 70 mm. At 1 MHz, US attenuation over the 70 mm chamber height was negligible in water, less than 1% in a glycerol solution with a viscosity of 10 mPa.s, and around 1.5% for a bulk viscosity of 23 mPa.s. At 2 MHz, the attenuation in US intensity was about 3% and 6.5% for bulk viscosities of 10 mPa.s and 23 mPa.s respectively. The increased ultrasound attenuation with increased frequency could be a reason for the lack of observable improvement in separation with an increase in frequency in the case of the 59% glycerol solution.

Figure 11. The effect of ultrasound frequency and the viscosity of the bulk phase on the attenuation of ultrasound in an acoustic chamber of length 70 mm.

The effect of emulsion droplet size and bulk phase viscosity on the maximum separation efficiency after 12 minutes of sonication at an ultrasound frequency of 1 MHz is summarised in Figure 12. As observed, the extent of separation achieved decreased with an increase in viscosity and a decrease in droplet size. In these experiments the maximum power ultrasound used was 54 W/L, which corresponds to an energy density of 1.7 J/m³. This energy density is much lower than those typically reported in literature. For example, Juliano et al.¹ used 5-25 J/m³ for separating fat from milk and Pangu and Feke³⁵ used around 55 J/m³ for separating canola oil-in-water emulsions. Even though separation efficiency decreasing with increased viscosity, this can be counteracted either by using longer sonication times or higher power.

Figure 12. The effect of emulsion droplet size and bulk phase viscosity on the separation efficiency achieved after 12 minutes of sonication at an ultrasound frequency of 1 MHz. The average droplet size for each experiment is annotated next to the corresponding data point.

4. Conclusions

The bulk phase viscosity, emulsion droplet size, power and frequency of ultrasound influenced the separation efficiency of mineral oil-in-water emulsions. An increase in the viscosity of the bulk phase decreased the separation efficiency of fine emulsions with small droplets, but only minimally affected coarser emulsions. The maximum separation efficiency for the fine emulsion (4.5-6 µm) decreased by almost 6 times, from 80 to 14%, when the viscosity was increased 23-fold (from 1 to 23 mPa.s). However, for the large droplet size (11-20 µm) emulsion, the maximum separation efficiency decreased by 1.5 times from 98 to 62% when the viscosity of the bulk phase increased 23 times. Conversely, increasing the ultrasound power intensity had little influence on the separation efficiency of coarse emulsions, while significantly improving the separation of fine emulsions. For the coarse emulsion (11 µm), nearly complete separation was observed that was independent of ultrasound power. For the fine emulsion (4.5 µm), the maximum separation increased from

36 to 79% when the ultrasound power was increased by five times from 10 to 54 W/L. Calculations showed that the time for droplets to reach nearest pressure anti-nodal plane of the ultrasound standing wave was influenced by the primary acoustic radiation force, and could be used to explain the influence of ultrasound power, emulsion droplet size and bulk phase viscosity on separation efficiency. COMSOL multiphysics simulations of emulsion droplets subjected to ultrasound standing waves showed band formation within the time scales calculated from analytical theory. The increase in frequency from 1 to 2 MHz significantly improved the separation efficiency for emulsions with small droplets from 36% to 86%. Band formation time scales from both analytical theory and simulations decreased with increased frequency, explaining the improved separation at the higher frequency. US frequency had no discernible effect on the separation of emulsions in the case of the 59% glycerol bulk phase regardless of droplet size or power density. This could be due to the increased attenuation of US in viscous systems at high frequency. Based on our study, it is suggested that high-frequency, low-intensity US standing wave separation is a suitable separation method for separating the emulsions with large drop size and low bulk phase viscosity.

5. Declarations

5.1 Availability of data and material

The data files for all data presented in the manuscript are available from the corresponding author upon request.

5.2 Supporting Information

Supporting information is provided in supplementary file. This information is available free of charge via the Internet at <https://eq4ZCgZolKFAAZLqGFNXtW5?domain=pubs.acs.org>.

Table S1. Physical properties of bulk and dispersed phases used in making model emulsions.

Table S2. Emulsion preparation conditions for different bulk phases and droplet sizes.

Figure S1. Geometry used in COMSOL® multiphysics (pressure acoustics combined with particles in fluid flow) simulations of emulsion droplets subjected to a 1 or 2 MHz US standing wave field at 10 W power.

Figure S2. COMSOL® multiphysics simulation of the emulsion droplets in 59% glycerol subjected to a 1 MHz US standing wave field at 10 W power.

Figure S3. COMSOL® multiphysics simulation of the emulsion droplets in 70% glycerol subjected to a 1 MHz US standing wave field at 10 W power.

Figure S4. The time required for two mineral oil emulsion drops suspended in bulk water-glycerol mixtures to coalesce due to the secondary acoustic force (Bjerknes force) when subjected to ultrasound standing wave field at 1 MHz.

Figure S5. The time required for coalescence of two adjacent mineral oil emulsion drops due to secondary forces (Bjerknes force) when subjected to ultrasound standing wave field at 1 MHz.

5.3 Competing interests

There are no competing or conflicts of interest to declare.

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