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Mathias Steinacher

École Polytechnique Fédérale de Lausanne

Esther Amstad (✉ esther.amstad@epfl.ch)

École Polytechnique Fédérale de Lausanne <https://orcid.org/0000-0002-9491-1010>

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Spray-assisted formation of micrometer-sized emulsions

Mathias Steinacher, Esther Amstad*

Soft Materials Laboratory, Institute of Materials, École Polytechnique Fédérale de Lausanne
(EPFL), 1015 Lausanne, Switzerland

E-Mail: esther.amstad@epfl.ch

Abstract

Emulsion drops with defined sizes are frequently used to conduct chemical reactions on picoliter scales or as templates to form microparticles. Despite tremendous progress that has been achieved in the production of emulsions, the controlled formation of drops with sizes of a few μm at high throughputs remains challenging. Drops of this size, however, are in high demand for example for many pharmaceutical, food, and material science applications. Here we introduce a scalable method to produce water-in-oil emulsion drops possessing controlled diameters of just a few microns: We fabricate calibrated aerosol drops and transfer them into an oil bath to form stable emulsions at rates up to $480\ \mu\text{l min}^{-1}$ of the dispersed phase. We demonstrate that the emulsification is thermodynamically driven such that design principles to successfully form emulsions can easily be deduced. We employ these emulsion drops as templates to form well-defined μm -sized hydrogel spheres and capsules.

1. Introduction

Emulsions are dispersions of two immiscible liquids that are applied in the food^{1,2}, cosmetic³, and pharmaceutical⁴ sectors to combine properties of both liquids in a single macroscopic phase or to disperse insoluble moieties in a media. Furthermore, emulsions are employed as templates to form particles⁵⁻⁷, capsules^{8,9} and foams^{10,11} that serve as carriers for active ingredients or living species. Emulsions are most commonly formed using high shear processes such as rotor-stator systems, pressure homogenizers or sonication¹². These methods produce emulsions at high throughputs but suffer from a poor control over the drop size, resulting in a broad size distribution of the emulsion drops. Moreover, the large amount of energy that is added to the system prevents these methods from processing sensitive materials. Drops of controlled sizes can be formed if minimal amounts of energies are added to the system, for example, by pushing one fluid through a membrane into a second immiscible one^{13,14}. Even a tighter control over the size of drops is achieved if they are formed in microfluidic devices albeit at a significantly lower throughput. Moreover, the resulting drops are larger, their diameters are typically in the range of 10-100 μm ¹⁵⁻¹⁸. Carriers produced from these drops are often too large to be applied in food, pharmaceutical, and many biomedical applications. Furthermore, the throughput of membranes and microfluidic devices decreases with decreasing drop size such that the production of smaller drops becomes increasingly time consuming and costly.

Emulsion drops with diameters of order 100 μm can be formed by consuming minimal amounts of energy if airborne aqueous drops are immersed into an oil bath. This can be achieved if drops are ejected into the air with a kinetic energy that is sufficiently high to overcome the surface tension of the oil bath such that they immerse into the oil, resulting in emulsions¹⁹. However, for smaller drops, the capillary forces exceed the inertial forces such that emulsion drops of a few micrometers

are difficult to form. To overcome this limitation, a thermodynamic driving force is required to transfer small aerosols into emulsion drops. This can be achieved by tuning the surface tensions of the liquids and air, namely that between the water and the air, the oil and the air and the water and the oil, respectively, γ_{wa} , γ_{oa} and γ_{wo} . If the spreading coefficient, defined as $S = \gamma_{wa} - (\gamma_{oa} + \gamma_{wo})$, is positive, airborne drops spontaneously immerse in the oil bath^{20,21}. Indeed, if two immiscible liquids that result in a positive S are chosen, the formation of emulsions is highly scalable if one liquid condenses from a gas phase onto the second one. Unfortunately, this method offers limited control over the drop size. Moreover, the water drops cannot be loaded with reagents, such that the number of applications of the resulting emulsion drops is very limited. Reagent-loaded airborne drops of tunable sizes³⁴ can readily be formed with surface acoustic waves (SAW)^{22–30}. Indeed, this method even allows the production of airborne drops containing living cells^{31–33}. However, SAW atomizers have never been used to fabricate calibrated emulsion drops.

Here we introduce a scalable emulsification technique that forms water-in-oil emulsions with diameters of only a few micrometers, a size range that is difficult to access with conventional microfluidic and membrane emulsification techniques. This is achieved using a SAW-based atomizer to form airborne aqueous drops of defined sizes and compositions that spontaneously immerse into an oil bath to form water-in-oil emulsions. We demonstrate that the emulsification process is thermodynamically driven. Hence, this process can be extended to a wide variety of surfactant and oil systems that fulfill the thermodynamic requirements. The resulting emulsions are used as templates to fabricate micrometer-sized hydrogel particles or capsules that can be used, for example, in the pharmaceutical, food, or cosmetic industry.

2. Results and Discussion

2.1. Emulsification

Key to the formation of emulsion drops with defined sizes, is the controlled generation of airborne drops. Such aerosol drops are formed with a SAW atomizer. To continuously and controllably atomize the liquid, we supply it to the piezoelectric device at constant fluid flow rates. To ensure an efficient atomization, we guide it to the location where it is atomized most efficiently using a microfluidic channel. The atomizer is operated at a frequency of 32.5 MHz with the spray plume directing downwards, towards the surface of an oil bath, as schematically illustrated in [Figure 1a](#). As a model system, we employ an aqueous phase containing 0.5 wt% of the surfactant Tween 80 as a dispersed phase and dodecane containing 0.5 wt% of the surfactant Span 80 as a continuous phase. Once the airborne aqueous drops impact the oil bath, they are spontaneously engulfed by the oil to form a water-in-dodecane emulsion. Because of the difference in the refractive indices of the two liquid phases and the size of the drops that is in the micrometer range, the emulsification is accompanied by a strong increase in turbidity, as exemplified in [Figure 1b](#) and [Supplementary Movie 1](#). The resulting emulsion drops have an average diameter of $5.7 \pm 2.5 \mu\text{m}$, as shown in the optical micrograph in [Figure 2a](#). This size is significantly below the average size of emulsion drops that can conveniently be formed in standard microfluidic devices. Yet, it is much larger than the size of emulsions formed by tip sonification, as shown in [Figure 2c](#). Hence, our SAW emulsifier enables the formation of calibrated emulsion drops in a size range that is difficult to achieve with other emulsification techniques. Importantly, these drops are stable for hours if stored at room temperature, as indicated by the unchanged diameter of the emulsion drops after they have been stored for 4 h in [Figure 2b](#). This timeframe allows a convenient conversion of drops into

microparticles or capsules, or their use as picoliter-sized vessels to conduct chemical reactions or high throughput screening assays.

The size of emulsion drops formed through many batch emulsification techniques strongly depends on the interfacial tension of the system and hence, the surfactant concentration in the oil phase. This dependence makes it difficult to tune the size of drops without altering their stability. The emulsification presented here bases on a fundamentally different principle such that we expect the drop size to be independent of the surfactant concentration. To test this expectation, we spray aqueous drops containing 0.5 wt% Tween 80, into an oil bath that is supplemented with a 10-fold higher surfactant concentration, 5 wt% Span 80. Indeed, the size of the resulting drops is within experimental error the same as that of drops containing only 0.5 wt% Span 80, as shown in [Figure 2d](#). By contrast, the size of drops strongly depends on the Span 80 concentration if the two fluids are emulsified through vortexing, as a comparison of [Figures 2e](#) and [Figure 2f](#) reveals. This dependence renders the size of drops formed through these shear-based bulk emulsification techniques sensitive to the surfactant choice. It adds another danger: If the surfactant combination is chosen to efficiently lower the interfacial tension, tiny emulsion drops spontaneously form, as shown in [Figure 2f](#). The number of these small drops grows with time, thereby preventing any control over the number and size of emulsion drops that form in the system. This is in stark contrast to our spray-assisted emulsification process where very low amounts of surfactants are sufficient to stabilize the drops. At these low surfactant concentrations, the spontaneous formation of these tiny drops is limited such that we possess a good control over the number and size of drops that form.

The size of airborne drops produced with SAW devices can be tuned in the range of 1 μm to 15 μm by controlling the operation frequency³⁴. To test if this is also the case for our emulsion drops,

we operate our SAW device at a frequency of 65 MHz and analyze the size of the resulting emulsion drops using optical micrographs. Indeed, if we increase the SAW operation frequency two-fold to 130 MHz, the size of the emulsion drops is decreased 2-fold, as a comparison of Figure 3a and Figure 3b reveals and summarized in the histogram in Figure 3c. These results indicate that the size of our emulsion drops inversely scales with the operation frequency of the SAW device such that it can be conveniently tuned. These findings suggest that aerosol drops are transformed into emulsion drops as an entity. Fragmentation of drops impacting an immiscible fluid surface is observed for high Weber numbers, defined as

$$We = \frac{\rho u^2 r}{\gamma}$$

here ρ is the density of the drop, u the drop velocity, r the drop radius and γ its surface tension³⁵. We is a dimensionless number that describes the ratio of the inertial and surface tension forces. To assess the likelihood that our drops are fragmented, we calculate We assuming $\rho = 1000 \text{ kg m}^{-3}$, $u = 0.1 \text{ m s}^{-1}$,³⁶ $r = 3 \text{ }\mu\text{m}$ and $\gamma = 43.7 \text{ mN m}^{-1}$. We find $We = 6.7 \times 10^{-4} \ll 1$. At such low We , we do not expect any fragmentation of the drops, because capillary forces predominate and inertial forces can be neglected, well in agreement with our observations

2.2. Mechanism of emulsion formation

We observe that emulsion drops robustly form if the density of the oil is below that of water such that the aqueous drops sediment to the bottom of the collection vial. To test if this density difference governs the emulsification process and thus our method is limited to light oils, we spray aqueous drops into a fluorinated oil, HFE 7500, that is much heavier than water, as shown in Figure 3d. To allow the drops to immerse into the oil and prevent their coalescence, we add 0.5% Krytox as a surfactant to the oil. The resulting drops display a similar size distribution as those sprayed

into dodecane, as can be observed by comparing the histograms in [Figure 3c](#) and [Figure 3e](#). This result indicates that the oil density is of minor importance to the emulsification process, illustrating the versatility of our system.

While we can successfully form water-in-oil emulsions, we cannot form the inverse. To understand this observation and thereby to define requirements for the system, we elucidate the emulsification process. Our results and calculations suggest that the size of the aerosol drops directly translates into the size of the emulsion drops such that we expect each impacting drop to immerse into the oil in its entirety. However, the fact that we cannot form oil-in-water drops indicates that not all drops immerse into the liquid they are sprayed onto. To understand the reason for this observation, we investigate the influence of the kinetic energy of the impacting drops. If the kinetic energy of the impacting aerosol drops is sufficiently high, they immerse into the oil because their energy is sufficient to overcome the surface energy penalty of the oil bath associated with this process.¹⁹ To test if the kinetic energy of the drops is also driving the emulsification presented here, we spatially separate the SAW atomizer from the oil bath using a 14 cm long tube to slow down the aerosol drops before they hit the oil surface. Despite the much larger spatial separation of the spraying unit and the oil surface, we observe the formation of tiny emulsion drops albeit at a lower yield because some airborne drops condense at the tube wall, as shown in [Figure S1](#) (Supplementary Information).

Our observations indicate that the immersion of airborne drops into the oil bath is not governed by their kinetic energy and instead dominated by the capillary forces, as indicated by the low We . Water drops spontaneously immerse into an oil bath if the spreading coefficient, defined as $S = \gamma_{wa} - (\gamma_{oa} + \gamma_{wo})$ is positive²⁰. In this case, the oil is spreading on the surface of the water drop, thereby engulfing it. To test if our emulsification relies on this principle, we quantify the surface

and interfacial tensions of the components involved using pendant drop tensiometry and use these values to determine S . For an aqueous phase containing 0.5 wt% Tween 80 dispersed in dodecane containing 0.5 wt% of Span 80, we find a positive spreading coefficient, 19 mN m^{-1} , as summarized in Table S2 (Supplementary Information), suggesting that our emulsification is thermodynamically driven. To test this hypothesis, we spray pure water into dodecane; this system has a negative spreading coefficient of -4 mN m^{-1} , as indicated in Figure 4a (i) and Table S2, such that we do not expect drops to immerse into the oil. Indeed, if we spray pure water into dodecane, we observe the formation of an aqueous film on top of the oil bath. As the film thickness grows, gravitational forces become significant and millimeter-sized emulsion drops eventually form, as shown in Figure 4b (i).

Our results suggest that the spray-assisted emulsification reported here is governed by thermodynamics such that its success can be predicted by calculating the spreading coefficient. The spreading coefficient is directly related to the interfacial tension between the water and the oil, which strongly depends on the type and concentration of surfactants contained in the system. However, the interfacial tension is independent of the location of the surfactant. To demonstrate this feature, we add 0.5 wt% Tween 80 to the aqueous solution and spray it onto a dodecane bath. The spreading coefficient of this system is 12 mN m^{-1} , as shown in Figure 4a (ii) and detailed in Table S2 (Supplementary Information), such that we expect this system to emulsify. Indeed, the small amount of surfactant present in the aqueous phase enables drops to immerse into the dodecane, in stark contrast to pure aqueous drops, as shown in Figure 4b-c (ii), confirming our hypothesis that a positive spreading coefficient is required to successfully form emulsions. However, because we do not have any surfactants in the continuous phase, the emulsion drops coalesce when they come in contact, as predicted by the Bancroft rule and indicated by Figure 4d

(ii). To prevent drop coalescence, we add Span 80 to the continuous phase; this addition increases the spreading coefficient of the system to 18 mN m^{-1} . Indeed, in the presence of Span 80 the emulsion drops do not only form, but they also remain stable for an extended amount of time, as shown in Figure 4b-d (iii). Similarly, we obtain a stable emulsion when the surfactant is only present in the oil, as shown in Figure S3 (Supplementary Information). These results indicate that in our emulsification process, the drop formation is decoupled from their stabilization, by analogy to the microfluidic emulsification, and in contrast to most bulk emulsification techniques. These results also explain why we failed to form oil-in-water emulsions: the high surface tension of water prevents us from identifying a system possessing a positive spreading coefficient.

The emulsification process presented here is controlled by thermodynamics. Nevertheless, kinetics is important as the engulfment process must be sufficiently fast to ensure drops are fully surrounded by oil before new drops arrive at the same location. We expect the engulfment kinetics to depend on the viscosity of the oil bath. To verify this expectation, we vary the oil viscosity between 1.5 and 24.5 mPa s by adding different volumes of mineral oil to dodecane. In all cases, the spreading coefficient is positive such that we expect emulsion drops to form, if we only consider the thermodynamic argument. However, large emulsion drops start to form at the oil surface if the oil viscosity is equal or higher than 4.2 mPa s, as shown in Figure 5. In these cases, the oil flow around the drop is too slow such that incoming drops hit some of their predecessors before they are fully surrounded by the oil such that the drops merge. Thereby, we lose any control over the drop size and obtain polydisperse emulsions. A significant dilution of the aerosol plume avoids drop coalescence on the oil surface even when viscous oils are employed. However, this comes at the cost of throughput. Our finding is in good agreement with theoretical studies that have identified a critical oil viscosity above which the immersion of an aqueous drop is

suppressed.³⁷ Hence, our results demonstrate that the system must fulfill two key requirements to controllably form emulsions: The spreading coefficient must be positive and the viscosity of the continuous phase must be below 4.2 mPa s.

2.3. Emulsion drops as templates

Calibrated emulsion drops are often used as templates for the synthesis of microparticles and capsules of well-defined sizes. Here we introduce a process that forms drops with diameters below 10 μm , significantly smaller than drops commonly formed with microfluidic devices. This size range is well-suited for many pharmaceutical, food, and material science applications. We take advantage of the possibility to load these drops with reagents to demonstrate their potential to serve as templates of calibrated micrometer-sized particles. We spray an aqueous solution containing 20 wt% poly-(ethylene glycol) diacrylate (PEG-DA) into a dodecane bath containing 0.5 wt% Span 80 and 2-Hydroxy-2-methylpropiophenone which serves as a photoinitiator. The emulsion drops are converted into microparticles by exposing them to UV light to crosslink the PEG-DA. The resulting microparticles possess an average size of $3.9 \pm 1.5 \mu\text{m}$ if the aqueous solution is atomized at a frequency of $f = 32.5 \text{ MHz}$. Even smaller particles can be produced if the solution is atomized at $f = 65 \text{ MHz}$, as determined from scanning electron microscopy (SEM) images shown in **Figure 6a-b** and summarized in the histogram in **Figure 6c**.

Single emulsions are attractive templates for the scalable fabrication of capsules if the solidification of reagents can be confined to the drop surface.³⁸ However, this approach is typically employed for emulsion drops with diameters in the range of 10-100s of μm whose surface to volume ratio is very small. We demonstrate that even micrometer-sized emulsion drops that possess a much higher surface to volume ratio can be employed as templates to fabricate capsules that still possess liquid cores: We produce aqueous drops encompassing tannic acid and spray them

into an oil bath containing ferric ions. Upon contact of the tannic acid with Fe^{3+} , complexes form at the interface, resulting in thin, rigid, ionically linked shells, as indicated by the dark color that appears only seconds after aqueous drops have been sprayed onto the oil surface, as shown in Figure 6d. They possess an empty core, as confirmed by the hollow cores seen in broken capsules in the SEM images in Figure 6e-f and are sufficiently stable to be re-dispersed in water, as shown in Figure 6g. Hence, these small drops can be used as templates to produce reagent-loaded micrometer-sized capsules that are stable for a prolonged time.

Aerosol drops can be produced with any atomizer. To highlight the versatility of our process, we employ an ultrasonic air humidifier to produce emulsions. We atomize an aqueous solution containing 0.5 wt% Tween 80 above an oil bath of dodecane containing 0.5 wt% of Span 80. The obtained emulsion drops have an average diameter of $8.2 \pm 3.7 \mu\text{m}$, as shown in Figure S4. Note that these atomizers are commercially available and easy to handle, yet, they offer an inferior control over the fluid atomization rate and drop size than the SAW atomizer.

Our results indicate that the emulsification process is thermodynamically driven such that we expect it to be robust and scalable. Indeed, we can increase the emulsification rate by raising the atomization rate, as shown in Figure 6h. Even if we employ a single SAW atomizer and an oil bath with a surface area of only 9.6 cm^2 , we achieve an emulsification rate of up to $480 \mu\text{l min}^{-1}$ considering the collection yield between 73 and 90%. Hence, a SAW nozzle can produce drops at much higher rates than individual microfluidic drop makers can, even though drops produced by the SAW device are much smaller. Note that the production of airborne drops is not limited to a single SAW device but could be parallelized if even higher throughputs are needed. These results illustrate the potential of our spray-assisted emulsification to produce micrometer-sized emulsion drops of defined sizes at throughputs sufficiently high to employ them as templates for

microparticles and capsules that can be used, for example, in the biomedical field, for food, and cosmetic applications.

3. Conclusions

We introduce a new process to form micrometer-sized emulsion drops of defined sizes. This is achieved with a surface acoustic wave-based device, which forms airborne aqueous drops that impact a surface of a continuous oil phase. If the spreading coefficient of the system is positive and the viscosity of the oil sufficiently low, it spontaneously and rapidly engulfs the drops, resulting in water-in-oil emulsions. These drops can be loaded with reagents, rendering them excellent templates for the formation of micrometer-sized particles and capsules. The scalable, gentle, low-energy SAW atomization process enables an energy-efficient encapsulation of sensitive materials such as cells or proteins. Importantly, the reported emulsification technique is not limited to the use of SAW atomizers but can be extended to any other type of atomizer. Thereby, it opens up new possibilities to employ micrometer-sized drops, particles, and capsules possessing well-defined and tunable sizes in applications that require large quantities of particles or capsules with diameters below 10 μm , as is frequently the case in cell-related studies, food and cosmetic applications.

4. Methods

Materials: Water (DirectQ, Merck Millipore, 25 °C 0.05 $\mu\text{S cm}^{-1}$), n-Dodecane (Sigma-Aldrich), Mineral Oil light (Sigma-Aldrich), Span 80 (TCI Chemicals), Tween 80 (Fisher BioReagents), HFE 7500 (3M, USA), FSH (Krytox 157 FSH, Chemours, USA), Poly(ethylene glycol) ($M_w = 700 \text{ g mol}^{-1}$) (Sigma-Aldrich), 2-Hydroxy-2-methylpropiophenone (97%, Sigma-Aldrich), Sodium dodecyl sulfate (SDS) ($\geq 95\%$, Roth), Tannic acid (Sigma-Aldrich), Iron acetylacetonate (99+%, Acros Organics), Phosphate-buffered saline solution pH 7.4 (PBS) (Gibco), Poly(dimethylsiloxane) (PDMS) (Sylgard 184, Dow Corning).

SAW atomizer: Focused interdigital transducers (IDT) with an eccentricity of 30° are patterned on a LiNbO_3 using a liftoff process. The excitation frequency of the 35 finger pairs is matched to 32.5 or 65 MHz. The electrodes are fabricated by vapor deposition of 5 nm of Ti followed by 200 nm of Al. Finally, the wafer is diced into $2 \times 3 \text{ cm}^2$ devices. A PDMS microchannel ($100 \times 40 \mu\text{m}^2$) is plasma bonded (Plasma Prep 2, Gala instruments) on top of these chips such that the shunt channel outlet is pointing at the SAW focal point to facilitate the fluid supply. The SAW atomizer is driven by a frequency generator (Siglent SDG 2122 X) attached to an amplifier (Mini-Circuits LZY-22+) and an oscilloscope (Siglent SDS 1202X-E) connected to the atomizer via a customized printed circuit board. Attenuators are mounted between the generator and the amplifier (3 dB, VAT-3+, Mini-Circuits) as well as the amplifier and the SAW device (3 dB, BW-S3W20+, Mini-Circuits). The atomizing fluid is supplied using a syringe pump (Cronus Sigma 1000, Labhut) and atomized with an output voltage of the function generator of around 1 V.

Commercial atomizer: A commercially available ultrasonic humidifier (Linuo Mini i9, Galaxus Switzerland) is employed to produce emulsions.

Emulsification: In a typical experiment an aqueous solution is atomized at a rate of 5 - 10 ml h⁻¹ above an oil bath with a surface area of 9.6 cm² at a distance of around 5 mm. The emulsion is imaged using an inverted microscope (Eclipse TS100, Nikon) equipped with a camera (XCG-CG240C, Sony).

Control emulsification: As a comparison, emulsions are produced by vortex mixing a continuous phase of 5 ml dodecane containing 0.5 or 5 wt% Span 80 and 0.5 ml of the dispersed aqueous phase containing 0.5 wt% of Tween 80 for 30 seconds. Furthermore, a continuous phase of 5 ml dodecane containing 0.5 wt% Span 80 and 0.5 ml of the dispersed aqueous phase containing 0.5 wt% of Tween 80 is emulsified with a sonication horn (Branson, 450 Digital Sonifier) for 30 seconds at 10% amplitude.

Interfacial tension measurement: A drop shape analyzer (DSA 30, Krüss) is used to measure the interfacial tension. Measurements are done as triplicates.

Viscosity measurements: A double gap geometry of stainless-steel cylinders with a diameter of 35 mm mounted on a rheometer (Discovery HR-3, TA Instruments) is used to measure the viscosity of dodecane-mineral oil mixtures. The container is loaded with 12 ml of solution and viscosities are determined at 25 °C and shear rates of 100 s⁻¹ by averaging the values over a period of 30 s. Triplicates are measured and averaged to obtain the final value of the viscosity.

Hydrogel particles: To fabricate PEG-DA particles we emulsify an aqueous solution containing 20 wt% PEG-DA into an oil bath of dodecane containing 0.5 wt% of Span 80 and 3 µl 2-Hydroxy-2-methylpropiophenone per ml of dodecane. Small hydrogel particles are produced by operating the SAW at an excitation frequency of 65 MHz whereas the SAW excitation frequency for the production of large particles is 32.5 MHz. The emulsion is subsequently exposed for 5 minutes to

UV light (Camag UV lamp 4 12 W). The polymerized particles are washed 2 times with ethanol, once with an aqueous solution containing 5 wt% SDS and 2 more times with pure water. The particles are dried on a silicon wafer and coated with a 4 nm iridium film (Quorum Q150) before imaging them on a field emission SEM (Merlin, Zeiss).

Microcapsules: We spray an aqueous solution of PBS containing 25 mg ml⁻¹ of tannic acid into an oil bath composed of dodecane containing 2 mM iron (III) acetylacetonate and 0.5 wt% of Span 80. The capsules are washed twice with isopropanol, once with an aqueous solution containing 5 wt% SDS and 2 more times with pure water before freeze drying them and analyzing them with SEM.

Emulsification rate: We quantify the emulsification rate by evaluating the weight increase of the oil bath as a function of time. Thereby, it is ensured no water drops coalescence on the walls of the oil bath. Triplicates are measured and averaged to obtain the final values.

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Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions**Competing interests**

The authors declare no competing interests.

Correspondence

esther.amstad@epfl.ch)

Figures

Figure 1: Spray-assisted emulsification. a) Schematic illustration of the emulsification process showing a SAW atomizer above an oil bath. b) Photographs of the oil bath (top) before, (middle) while and (bottom) after 8 minutes of emulsification.

Figure 2: Optical micrographs of water-in-oil emulsion drops. a, b) Optical micrographs of aqueous drops that have been sprayed into an oil bath containing 0.5 wt% Span 80 acquired a) immediately after the production and b) after 4 hours of storage. c) Emulsions produced by tip-sonication. d) Optical micrographs of aqueous drops hat have been sprayed into an oil bath containing 5 wt% Span 80. e, f) Emulsion drops produced through Vortex mixing with oil containing e) 0.5 wt% Span 80 and f) 5 wt% Span 80.

Figure 3: Controlling the drop size. a, b) Optical micrographs of emulsion drops formed from airborne drops that have been produced with the SAW atomizer operated at a frequency of a) 65 MHz and b) 32.5 MHz. c) Size distribution of the resulting drops. d) Optical micrograph of water-in-HFE 7500 emulsion produced with a SAW excitation frequency of 32.5 MHz with e) the resulting drop size distribution. All histograms are created from $N > 450$ measured drops.

Figure 4: Influence of spreading coefficient, S , on emulsification. a) Summary of the spreading coefficient of three different systems. b-d) Photographs of emulsions b) while being formed, c) immediately after they have been formed and d) after they have been stored for 20 min. e) Schematic illustration of the emulsification process. (i) Water drops are sprayed onto a dodecane surface. S of this system is negative such that water drops coalesce at the surface of the oil until the water layer becomes too thick and large water drops start to pinch off due to gravitational forces. (ii) Water drops containing 0.5 wt% Tween 80 are sprayed onto a dodecane surface. S of this system is positive such that emulsions form. Because of the lack of any surfactant in the continuous phase, these emulsion drops coalesce with time. (iii) Water drops containing 0.5 wt% Tween 80 are sprayed onto the surface of dodecane containing 0.5 wt% Span 80. The system has a positive S such that emulsions controllably form. The presence of surfactants in the continuous phase kinetically stabilizes them such that they remain stable for at least 20 minutes.

Figure 5: Influence of the oil viscosity. Top: Photographs of emulsions composed of aqueous drops containing 0.5 wt% Tween that are dispersed in dodecane that has been mixed with different concentrations of mineral oil $\phi_{\text{Mineral oil}}$. Bottom: Viscosity η of dodecane-oil mixtures. The error calculated as the standard deviation is within the size of the symbols. To controllably emulsify, the oil viscosity must be below the experimentally determined dashed line.

Figure 6: Conversion of emulsion drops into microparticles and microcapsules. a-c) SEM micrograph of PEG-DA hydrogel particles produced with a SAW excitation frequency of a) 65 MHz and b) 32.5 MHz with c) their size distribution ($N > 380$). d) Photograph of the oil bath (left) before and (right) after producing tannic acid-based microcapsules with e, f) SEM micrographs of the freeze-dried microcapsules and g) an optical micrograph of the resulting microcapsules dispersed in water. h) Measured (symbols) and theoretical limit (--) of the emulsification rate when water is atomized at (●) 5 ml h^{-1} , (■) 10 ml h^{-1} , (▲) 20 ml h^{-1} and (◆) 5 ml h^{-1} . The error calculated as the standard deviation is within the size of the symbols.

Figures

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