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Droplet formation and growth mechanisms in reaction-induced spontaneous emulsification of 3-(trimethoxysilyl) propyl methacrylate

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Abstract

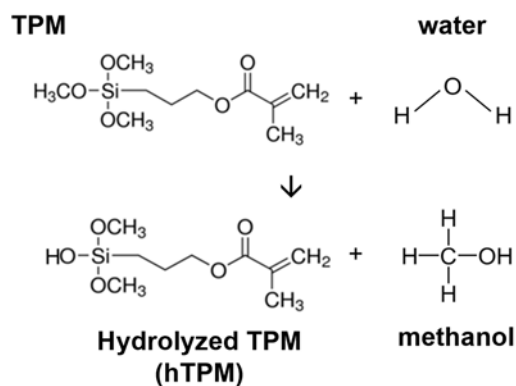
Spontaneous emulsification of 3-(Trimethoxysilyl) Propyl Methacrylate (TPM) can produce complex and active colloids, nanoparticles, or monodisperse Pickering emulsions. Despite its applicability in particle synthesis, the nucleation and growth mechanisms of TPM emulsions are still poorly understood. We investigate droplet formation and growth of TPM in aqueous solutions under quiescent conditions. Our results show that in the absence of stirring the mechanisms of diffusion and stranding likely drive the spontaneous emulsification of TPM through the formation of co-soluble species during hydrolysis. In addition, turbidity and dynamic light scattering experiments show that the pH modulates the growth mechanism. At pH 10.1 the droplets grow through Ostwald ripening while at pH 11.5 the droplets grow via monomer addition. Adding surfactants (Tween, SDS, or CTAB) leads to sub-100 nm droplets that are kinetically stable. The growth of Tween droplets occurs through addition of TPM species while keeping the number density of droplets constant. In addition, in the presence of the ionic surfactant SDS electrostatic repulsion between the solubilized TPM species and SDS leads to a significant increase in the number density of droplets as well as additional nucleation events. Finally, imaging of the solubilization of TPM in capillaries show that in the absence of surfactant, TPM hydrolysis is likely the rate-limiting step for emulsification, whereas the presence of silica particles in the aqueous phase likely act as catalyst of TPM hydrolysis. Our experiments highlight the importance of diffusion and solubilization of TPM species in the aqueous phase on nucleation and growth of droplets.

1. Introduction

Organosilica particles are increasingly being used for applications in catalysis¹, biosensing², or optoelectronics.³⁻⁴ Advantages of organosilica particles include the presence of silanol groups that aid colloidal stability as well as functional organic groups that can be used for modifications in biomedical applications.⁵ Organosilica particles are also less dense and more porous than silica due to the lower degree of siloxane condensation.⁶⁻⁷ Many studies report facile synthesis methods to create organosilica particles of various shapes and sizes.⁸ Specifically, spontaneous emulsification of 3-(Trimethoxysilyl) Propyl Methacrylate (TPM) can produce complex and active colloids.⁹ Spontaneous emulsification of TPM also forms monodisperse Pickering emulsions in aqueous nanoparticle dispersions,¹⁰ including isotropic core-shell particles¹¹ or anisotropic Janus particles.¹²⁻¹³ Despite its prevalent use in particle synthesis, the nucleation and growth mechanisms of TPM emulsions are still poorly understood.

The mechanism for TPM droplet formation is attributed to the hydrolysis and condensation of the TPM molecules in the aqueous phase (see **Fig. 1**). In the presence of water, TPM hydrolyzes at all pH conditions, with the slowest reaction rate around pH 4 (**Fig 1a**).¹⁴ Hydrolyzed TPM molecules can then undergo a condensation reaction to form a dimer through a siloxane bridge (**Fig. 1b**).¹⁵ Additional condensation reactions can lead to TPM oligomers ranging from trimers to octamers, but the next two methoxy groups on TPM hydrolyze at a slower rate.¹⁶⁻¹⁹ The slowest condensation rate is at pH 6, and increases as the solution becomes either alkaline or acidic, but is highest in alkaline conditions.¹⁵ TPM hydrolysis is known to be an essential step in the droplet formation process because TPM spontaneous emulsification has only been observed at alkaline (> pH 9.8) and acidic (< pH 4) conditions. It is hypothesized that hydrolyzed TPM molecules condense into oligomers that supersaturate, resulting in droplet nucleation.²⁰⁻²² The presence of methanol (a by-product of TPM hydrolysis) during TPM emulsification supports this hypothesis.²³ The mechanism is also analogous to the Stöber process,²⁴ and a similar mechanism was used to describe spontaneous emulsification of polydimethyl siloxane.²⁵ However, hydrolysis and condensation alone are not sufficient for spontaneous emulsification. In particular, spontaneous emulsification has not been reported for most organosilanes possessing hydrolysable and condensable groups, nor for tetraethyl orthosilicate.²⁶⁻²⁷ Other factors such as agitation, sudden change in solution pH, or stabilizing agents appear to play a role in the initial droplet size distribution, and thus need further investigation.²⁸

(a) Hydrolysis of TPM



(b) Condensation of hydrolyzed TPM

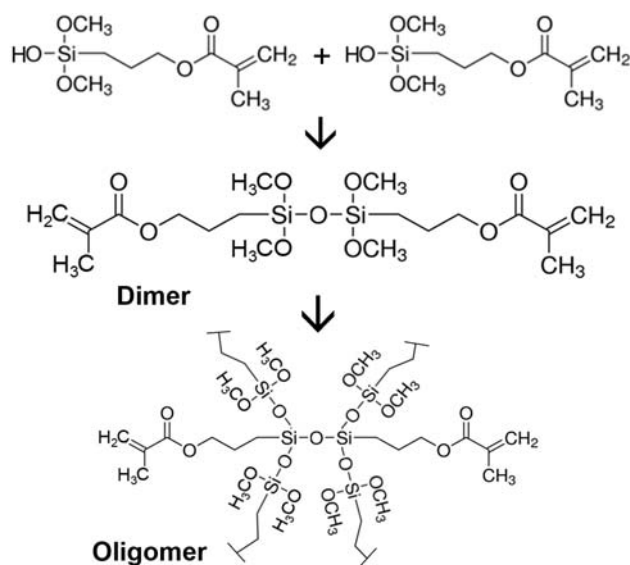


Figure 1. TPM reactions in the presence of water. (a) Hydrolysis of the first methoxy group to form hydrolyzed TPM and methanol. (b) Condensation of two hydrolyzed TPM molecules to form a dimer. Further condensation due to hydrolysis of the second and third methoxy groups can lead to TPM oligomers.

Other material systems where a chemical reaction at a fluid interface leads to spontaneous emulsification suggest that additional mechanisms could lead to TPM emulsification. In crude oils, interfacial reactions produce surfactants leading to ultralow interfacial tensions.²⁹⁻³¹ Ultralow interfacial tensions facilitate mechanical perturbations and droplet pinch-off from the interface. In addition, Nishimi et al. observed spontaneous emulsification when a reaction at the interface changed the solubility of the surfactants originally dissolved in the oil phase.³² The solubilization of the surfactant leads to water nucleation in the oil phase as well as oil supersaturation and oil droplet nucleation in the aqueous phase. Another example is the transesterification of triglycerides where many reaction products (mono-,

diglycerides, biodiesel) increase the miscibility of the original contacting fluids and cause emulsification.³³⁻
³⁴ More generally, mixing of multicomponent systems *via* diffusion in the interfacial region can lead to local supersaturation and droplet nucleation, in a process analogous to the Ouzo effect.³⁵⁻³⁶ The possible role of interfacial diffusion and mixing on TPM emulsification remains to be investigated.

Investigation of droplet growth during the spontaneous emulsification of TPM is limited. There are multiple possible mechanisms for droplet growth in emulsions. For example, once formed, droplets can grow through coalescence or through diffusion of solute between droplets (Ostwald Ripening).³⁷⁻³⁹ For a given mass of dispersed phase both coalescence and Ostwald Ripening result in a cubic growth of the droplet diameter over time and a decrease in the droplet number density over time.⁴⁰⁻⁴¹ Additional growth mechanisms could also include droplet growth due to a constant flux of solute (here the hydrolysis of TPM). Constant flux of hydrolyzed TPM could lead to additional nucleation events, similar to the aggregative growth model for silica particles.⁴² Droplets can also grow through addition of TPM species adsorbing to the droplet surface, similar to the La Mer model.⁴³⁻⁴⁶ The presence of surfactants or other stabilizing agents also adds complexity to the droplet growth because these additives limit droplet coarsening and coalescence.⁴⁷⁻⁴⁹ Surfactants also lower the interfacial tension and decrease the driving force for Ostwald ripening, but micelles may increase ripening by acting as shuttling vessels between droplets.^{37 48}

Here we investigate the nucleation and growth mechanisms of TPM droplets in alkaline aqueous solutions. We first investigate droplet formation and growth in the absence of stabilizing agents. We then study how the presence of surfactants or silica nanoparticles in the aqueous phase modifies droplet formation and growth. We propose that TPM droplet nucleation occurs through the production of co-soluble species at the oil-water interface, as in diffusion and stranding. After nucleation, the droplets primarily grow through TPM addition limited by TPM conversion to the aqueous phase as controlled by the solution pH. We then investigate the role of surfactants (Tween, SDS, and CTAB) on droplet formation and growth to determine the mechanisms for droplet growth and the possible contribution of electrostatic interactions between the surfactant and TPM species. Finally, we investigate droplet formation when silica particles are dispersed in the aqueous phase.

2. Materials and Methods

Materials. Sodium chloride (NaCl), sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), Ludox AS-40 Silica, and RBS 35 solution concentrate were purchased from Sigma-Aldrich and used as received. 3- (Trimethoxysilyl) Propyl Methacrylate (TPM, 98%) was also purchased from Sigma-Aldrich and stored under nitrogen. Nochromix crystals were purchased from Sigma Aldrich and mixed into 2.5 L of sulfuric acid purchased from Fisher Scientific. Sodium hydroxide (NaOH), Tween 20, and

methanol were purchased from Fisher Scientific. All solutions were prepared from deionized (DI) water with 18.2 M Ω cm resistivity using a Millipore Filtration System (Milli-Q Academic) at room temperature (22 °C).

Emulsification. Cuvettes were cleaned by soaking overnight in isopropanol. Before use, cuvettes were soaked for 20 min in 50:50 sulfuric acid dilution with deionized water. Cuvettes were rinsed thoroughly with DI water before soaking in 1 M NaOH solution for another 20 min. Cuvettes were rinsed with DI water 30X and dried with nitrogen before adding pH adjusted aqueous solution. Aqueous solutions were titrated to desired pH using sodium hydroxide. Sodium chloride is then added to maintain a constant ionic strength of 15 mM for all pH solutions. To start the emulsification of TPM, the aqueous solution is aliquoted into clean quartz cuvettes. A drop of TPM is deposited at the air-water interface using a polypropylene pipette tip. The cuvettes are immediately capped. When the cuvettes are not being imaged, they are stored in a dark, vibration-free environment.

Polymerization. TPM droplets are polymerized via radical polymerization using AIBN as the initiator. About 1 mg/mL of AIBN is added to the emulsion vial. After gentle mixing, the emulsion vial was loosely capped and placed inside an 80 °C oven for at least 10 h.

Phase diagram. The binodal curve was determined through by turbidity analysis using the titration procedure under isothermal conditions.^{33, 50} Samples started along the water-TPM axis and agitated to form a turbid emulsion phase. Methanol was then added dropwise to the solution and lightly agitated to fully mix. The composition where the solution became homogeneous was labeled as a point on the binodal curve.

Turbidity measurements. Solution absorbance was measured using a Cary 300 UV-vis spectrophotometer. Turbidity (τ) was calculated from absorbance using the equation $\tau = 2.303 \frac{A}{l}$,⁵¹ where A is the measured absorbance at 450 nm and l is the path length (1 cm).

Dynamic Light Scattering (DLS). Droplet diameters and zeta-potential were measured using a Zetasizer Nano-ZS (Malvern Instruments). For *in situ* size measurements, emulsions were prepared in quartz cuvettes to a total volume of 1 mL. After the TPM was deposited at the air-water interface, the cuvette was placed in the DLS and continuous measurements were taken until the oil was fully emulsified using back scattering. For zeta-potential measurements, emulsion samples were prepared in quartz cuvettes and transferred to folded capillary cells at fixed time intervals. All droplet sizes are reported in diameter and are the average of at least three measurements. The error bars in all plots are derived from the standard deviation of the droplet diameter and zeta potential for at least 3 trials. The polydispersity index (PDI) obtained from DLS measurements is the relative variance of the distribution described as $PDI = (\text{standard deviation/average size})^2$. Here we only report droplet diameters when $PDI < 0.2$.⁵²

Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR). Measurements were taken in absorbance mode on a Varian 660-IR spectrometer with a DTGS detector. To monitor the TPM droplet composition with time, aliquots of emulsified TPM were removed from the aqueous phase with care taken not to disturb the TPM drop still present at the air-water interface. The emulsion was centrifuged at 14,500 rpm using an Eppendorf Minispin Plus for 20 minutes. After centrifugation, the supernatant was removed and discarded. The droplets were dried in a chemical hood to break the emulsion and remove any excess water. The final TPM solution is deposited onto the ZnSe crystal on the ATR attachment.

Volumetric conversion measurements. To evaluate the rate of TPM conversion into the aqueous phase, 2 mm ID capillary tubes from VitroComm were used to maintain a fixed interfacial area and monitor TPM volume change. Capillaries were cleaned according to the protocol described above for quartz cuvettes. Volume change was calculated using ImageJ and assuming a symmetric distribution of TPM in the capillary.

Optical Microscopy. Rectangular capillaries with 0.4 mm and 2 mm inner diameters were purchased from VitroCom and cleaned by a three-step sonication protocol with acetone, isopropanol, then DI water solutions. The capillaries were then submerged in Nochromix sulfuric acid solution for 20 minutes. Following a thorough rinse with DI water, the capillaries were submerged in 1 M NaOH solution for 20 minutes. Capillaries were rinsed with DI water and completely dried using compressed air before use. To fill the capillary, the end is first sealed with epoxy. Then the capillary is filled about halfway with aqueous solution. Finally, 10 μ L of TPM are gently added to the air-water interface and the capillary is sealed with epoxy. The capillaries are observed on a Zeiss Axio Observer.A1 with a 40X objective or using a UI-3040LE-M-GL camera and ImageJ acquisition software.

3. Results and Discussion

3.1 Droplet formation

We characterize emulsification of TPM under quiescent conditions. A fixed volume of TPM is deposited on top of water in a cuvette in the absence of agitation, and without any additional stabilizing agents (surfactant or nanoparticles), see **Fig 2a**. Over time, droplet formation in the aqueous phase leads to an increase in solution turbidity, seen by the cuvette images in **Fig. 2b**. We observe that the solution becomes turbid at a distance from the interface (towards the bottom of the cuvette). In addition, closer inspection of the interfacial region using optical microscopy clearly indicates the presence of aqueous droplets forming in the TPM phase (**Fig. 2c**). Droplets were present in both the oil and aqueous phase for all pH investigated (pH 10.1 to pH 11.9). We also observe that the elapsed time after which we first observe

turbidity in the aqueous phase decreases with an increase in pH. Similarly, we also find that the elapsed time when we first notice the presence of aqueous droplets in the oil phase decreases with an increase in pH (**Fig. 2d**). Note here that the methods to identify the onset of emulsification in the oil and water phases are different (turbidity vs optical microscopy). The resolution limit for the optical microscopy measurements only allows us to observe larger droplets ($\sim 1\ \mu\text{m}$), while the detection limit for turbidity depends both on the droplet diameters and volume fraction. Therefore, while **Fig. 2d** clearly shows that the trend with pH is the same for both phases, we cannot compare the absolute elapsed time between both phases.

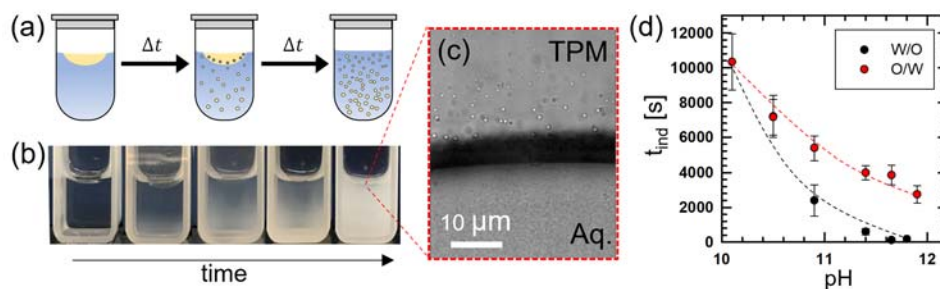


Figure 2. pH-dependent droplet nucleation occurs on both sides of the oil-water interface. (a) Schematic of the experiments showing droplet formation over time. (b) Images of 10 μL of TPM emulsifying into pH 11.5 solution over 100 minutes. (c) Microscopy image of droplet formation on both sides of the oil-water interface after 45 min in pH 11.5 solution. (d) Dependence on solution pH of the induction time of W/O (black) droplets and O/W (red) droplets in 15 mM ionic strength and $\Phi = 0.01$ for O/W emulsions. Dotted lines are to guide the eye.

We investigated if droplet pinch-off from the interface occurs for spontaneous emulsification of TPM. Droplets formed through pinch-off from the interface should have a similar composition to the bulk oil phase.⁵³ We investigated if the presence of a water-insoluble molecule mixed in the oil phase (hexadecane, C16) would be incorporated in the emulsified phase. Hexadecane is soluble in TPM but insoluble in both water and methanol.⁵⁴ Therefore, hexadecane acted as a tracer molecule⁵⁵ dissolved in the TPM phase to identify droplet pinch-off from the interface. We found that mixtures of TPM and C16 emulsified spontaneously, but that residual oil was leftover at the air-water interface (**Fig. 3a**). Using FT-IR spectroscopy we determined if the emulsion droplets contained C16. The droplets isolated from emulsions of oil mixtures with $\Phi_{\text{C16}} = 0.9$ and $\Phi_{\text{C16}} = 0.5$ showed identical compositions (**Fig 3b**). In contrast, the residual oil showed stretching bands from the CH_2 ($2850\ \text{cm}^{-1}$) and CH_3 ($2920\ \text{cm}^{-1}$) that are prominent in C16.⁵⁶ Therefore, the residual oil phase mostly contained C16.

We used the IR spectra to quantify the C16 to TPM ratio in the emulsion droplets using the ratio of $\text{C}=\text{C}$ ($1637\ \text{cm}^{-1}$) *str* to CH_2 ($1378\ \text{cm}^{-1}$) *def* bands (**Fig. 3c**).⁵⁷⁻⁵⁹ We see that the composition of the

emulsified phase is unaffected by the presence of C16 in the initial oil phase (red points). We also observe that TPM is absent from the residual oil phase (star points). It is clear that C16 remains phase separated at the air-water interface after TPM emulsification. Emulsification through droplet pinch-off typically necessitates ultralow or negative interfacial tension.^{31, 60-61} We obtained values for the interfacial tension that varied between 3.5 and 11.8 mN/m around the onset of emulsification (**Fig. S1**). The emulsification process led to noise in the interfacial tension measurements but the interfacial tension was too high for droplets to form via pinch-off events.³⁰ Combined, these results suggest that partial miscibility in water of all components in the oil phase is necessary for emulsification.

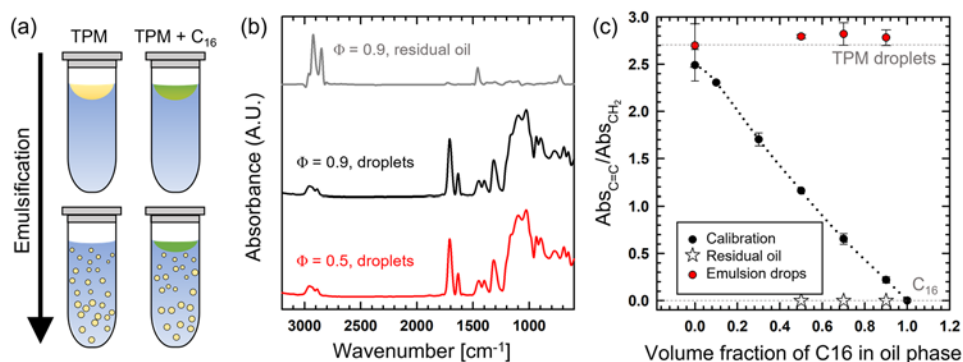


Figure 3. Hexadecane in oil mixtures is not present in the emulsion droplets. (a) Schematic of TPM emulsification with and without hexadecane (C16) shown in green. (b) FT-IR spectra of the droplet phase (black and red) as well as the residual oil phase (gray) after complete emulsification of TPM. The droplet phases for two TPM:C16 ratios are shown. (c) Ratio of the absorbance at the C=C *str* and CH₂ *def* bands for unreacted TPM-C16 mixtures (black circles), the leftover oil after complete emulsification (white stars), and the emulsion droplets isolated from the aqueous phase (red circles). Dotted lines indicate the ratios corresponding to pure TPM emulsion droplets (top) and pure C16 (bottom).

Diffusion and stranding has been observed in a number of oil-water systems with various salts, surfactants, and solvents to facilitate supersaturation.⁶²⁻⁶⁷ Droplet nucleation occurs when the local composition becomes unstable, which can be identified through the phase diagram of the solution components. When spontaneous emulsification occurs through diffusion and stranding, a water-in-oil emulsion is often observed simultaneously with the oil-in-water emulsion, and the oil-in-water emulsion appears a certain distance away from the oil/water interface.^{32, 61} We also observe that the oil droplets appear a distance away from the oil-water interface (**Fig. 2b**) and the presence of aqueous droplets in the oil phase. These two observations suggest that diffusion and stranding might be the mechanism for emulsification of TPM under quiescent conditions (see illustration in **Fig. 4a**). Diffusion and stranding requires a third component that is miscible in both the oil and aqueous phases. Methanol produced from the hydrolysis of TPM as well as hydrolyzed TPM (hTPM)⁹ are both completely soluble in water and could act as the co-

soluble species. Hydrolysis would lead to an increased concentration of hTPM and methanol at the interface, facilitating TPM and water diffusion along their concentration gradients across the oil-water interface. Then, further diffusion of methanol and hTPM away from the interface could lead to the supersaturation of TPM species (oligomers or unreacted TPM) in the aqueous phase and supersaturation of water in the oil phase.

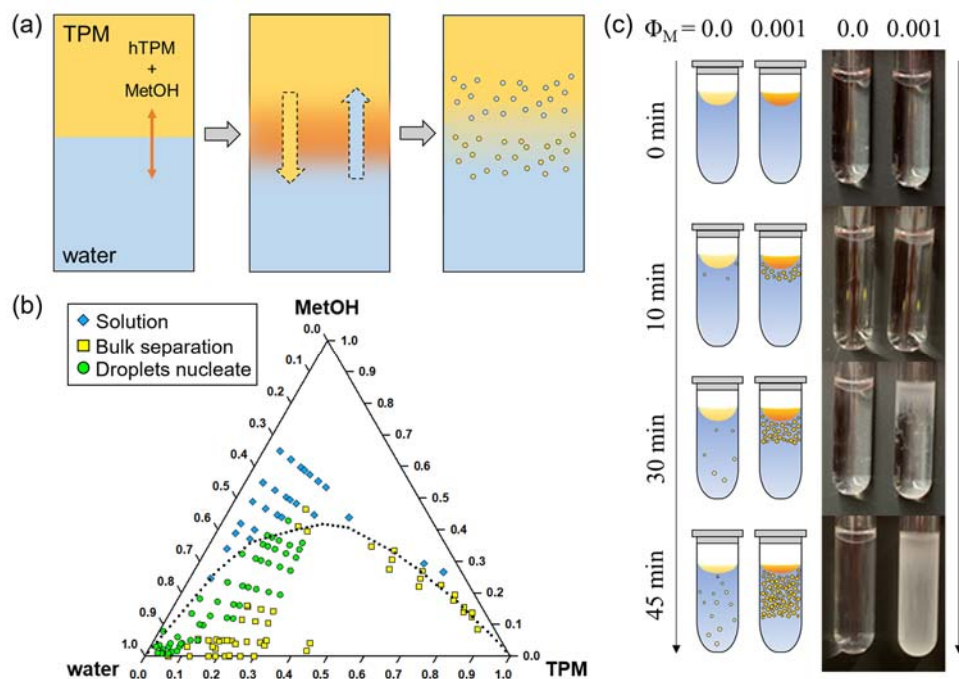


Figure 4. Local supersaturation driven by solvent production at the oil-water interface. (a) Schematic of reaction-induced supersaturation of TPM in the aqueous phase and water in the TPM phase. (b) Ternary phase diagram between water, TPM, and methanol. Black dotted line shows the binodal. Symbols indicate the solution phase behavior: complete mixing (blue diamonds), bulk separation through spinodal decomposition (yellow squares) and droplet nucleation (green circles). All solutions were mixed at pH 5.6. (c) Effect of added methanol on the onset of turbidity. First column: schematic of a pure TPM drop (yellow) emulsifying from the air-water interface beside a TPM drop with added methanol (orange). Second column: corresponding images of TPM drops emulsifying over 45 minutes at pH 11.

We investigated the phase behavior of ternary mixtures of TPM, methanol and water to determine if there exists a composition where the unstable solution phase separates through droplet nucleation (**Fig. 4b**). We used pH 5.6 water to limit the effects of TPM hydrolysis on the phase behavior between the three components.¹⁵ Methanol, a byproduct of TPM hydrolysis, increases the solubility of TPM in water, as indicated by the binodal curve (black dotted line in **Fig. 4b**). Under the binodal curves lies the phase envelope, where the solution compositions are unstable and phase separate and form droplets. The region where phase separation occurs through droplet nucleation is shown as green circles. For spontaneous

emulsification to occur, the local composition near the interface must fall into this region, confirming that diffusion and stranding is a possible mechanism for TPM emulsification. Note that concentration gradients are possible in the absence of agitation. Locally the solution composition could cross the binodal even if globally the overall composition would not phase separate.

The mechanism of diffusion and stranding is consistent with the pH-dependence of emulsification.⁶⁸ As the pH increases, the hydrolysis reaction produces methanol at the interface, which would facilitate emulsification. Moreover, we observe that by adding excess methanol to the oil phase, the emulsion onset time decreases despite reports that methanol decreases the condensation rate (**Fig. 4c**).¹⁸ After 45 min, the pure TPM droplet shown on the left has yet to emulsify into the pH 11 solution, while the TPM-methanol mixture ($\Phi = 0.001$) (right) shows significant turbidity, indicating droplet formation. Since methanol may decrease silane condensation rates, the increase in emulsification in the presence of excess methanol can be attributed to the diffusion of methanol in the aqueous phase and stranding of TPM.

Droplet growth without stabilizing agents

We monitor TPM droplet growth *in situ* using DLS and UV-vis spectroscopy to determine the droplet size and concentration over time, while keeping the cuvettes agitation-free. We selected two aqueous phase pHs (pH 10.1 and pH 11.5) to be below and above the pKa of the silanol groups on hydrolyzed TPM (**Fig. 4c**).²⁸ Through DLS, we obtain the droplet size (D) and zeta potential (ζ). Through UV-vis absorbance we measure turbidity. For dilute emulsions with low polydispersity (< 0.2)⁶⁹ we can combine DLS and turbidity data to obtain the time-resolved number density of droplets and their volume fraction (ρ and Φ , respectively). See Supporting Information S2 for more information on the data analysis. The data is also summarized in **Table 1**, where we report the induction time (t_{ind}), defined here as the earliest time after which droplets can be detected in DLS. Note that it is unlikely that t_{ind} is the nucleation induction time. DLS requires sufficient signal to accurately report the droplet size and smaller droplets require higher number densities than larger droplets to achieve reliable measurements.⁶⁹

We observe a decrease in t_{ind} with increasing solution pH (**Table 1**). More specifically, the induction time decreases by a factor of three when the pH of the aqueous solution increases from pH 10.1 to pH 11.5. The decrease in t_{ind} with increasing pH is consistent with the TPM reactions (hydrolysis or condensation) being the limiting step in droplet formation. While the onset of emulsification is slower at pH 10.1, the earliest droplet size detected is nearly the same at both pH. The same droplet size at induction for the two pHs investigated could be due to a similar critical condition (supersaturation).

Table 1. Characterization of droplet formation.

pH	Stabilizing agent	Φ_0	Concentration [mM] (ω) ^a	Initial droplet size [nm]	Induction time ^b [s] x 10 ³
10.1	None	0.01	--	207 ± 18	7.0 ± 0.6
	Tween	0.01	2 (21)	14 ± 1	8.9 ± 2.9
	SDS	0.01	6 (7)	50 ± 4	21.6 ± 3.8
	CTAB	0.01	0.3 (140)	304 ± 62	1.8 ± 0.3
	SiO ₂	0.01	3 w/w%	260 ± 15	6.0 ± 1.2 (1.8 ± 0.3) ^c
11.5	None	0.01	--	183 ± 13	2.1 ± 0.4
		0.005	--	130 ± 22	2.0 ± 0.3
	Tween	0.005	1 (21)	14 ± 1	3.8 ± 0.3
		0.01	1 (42)	16 ± 2	3.6 ± 1.0
			2 (21)	16 ± 1	2.9 ± 0.9
	SDS	0.03	3 (42)	15 ± 1	1.4 ± 0.3
	CTAB	0.01	0.3 (140)	19 ± 1	2.0 ± 0.2
	SiO ₂	0.01	3 w/w%	175 ± 13	8.4 ± 0.4 (0.2 ± 0.06) ^b
	SiO ₂ + Tween	0.01	3 w/w% + 1 (42)	45 ± 5	10.2 ± 0.6 (4.2 ± 0.6) ^b

^a ω is the molar ratio of TPM to surfactant^b Time at which first droplet is detected in DLS measurements^c Induction time determined by onset of turbidity (visual inspection)

To compare the droplet growth rate at the two pHs we shift the time axis by their respective induction time (**Fig. 5**). We see that the growth rate at the early stage for both pH is nearly the same. When the droplets reach approximately 500 nm in diameter the droplets at pH 10.1 continue to grow while the growth at pH 11.5 slows down until all the oil is emulsified (and the droplets remain monodisperse, PDI < 0.2), see **Fig. 5a**. For pH 10.1 the droplets initially have a narrow size distribution, but the polydispersity increases rapidly over time, and we cannot characterize the growth beyond approximately 1% of the TPM conversion due to the large droplet size. For both pHs, the TPM droplets are not kinetically stable and their size continues to

grow after the TPM reservoir is fully depleted. For example, the droplet size increases to 1240 ± 450 nm after 48 h and eventually aggregate and sediment.

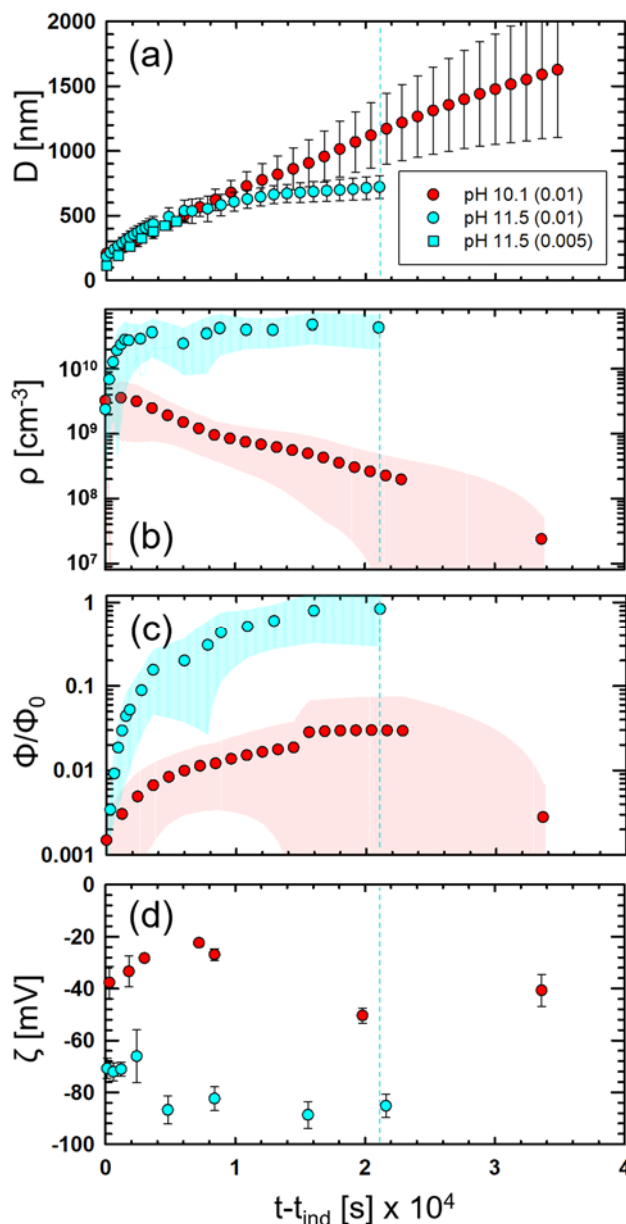


Figure 5. Droplet growth curves without stabilizing agents. (a) Droplet diameter at pH 10.1 (red) and pH 11.5 (cyan). The value in parenthesis indicates Φ_0 . (b) Number density of droplets calculated from turbidity and DLS measurements. (c) Volume fraction of TPM emulsified into the aqueous phase as a fraction of the total TPM added. (d) Zeta potential of TPM droplets. Dashed cyan line indicates the average time for complete emulsification of TPM at pH 11.5, $\Phi_0 = 0.01$.

We gain insight in the growth process by comparing the number density of droplets over time and across pH (**Fig. 5b**). At the induction time, the number density is similar between the two pH conditions. Shortly after induction (20 min) for pH 11.5 the number density has increased by an order of magnitude

and then remains relatively constant afterwards. In contrast at pH 10.1 the number of droplets decreases exponentially over time. At pH 10.1 we also see a decrease in volume conversion at very long times (~ 9 hrs), likely due to aggregation and sedimentation, consistent with the observation of large droplets at the bottom of the cuvette (below the optical path of the detector). The combination of rapid growth in droplet diameter with a decrease in number density at pH 10.1 suggests coalescence or Ostwald ripening, especially considering the much slower conversion of TPM molecules based on the conversion rate (**Fig. 5c**).

Coalescence occurs from droplet collisions in solution, while Ostwald ripening is the result of finite solubility of the dispersed phase.⁷⁰ Zeta potential measurements allow us to assess the colloidal stability of the emulsion droplets (**Fig. 5d**). Throughout the droplet growth the droplets have negative zeta potentials and become more negative over time. At pH 11.5, the initial zeta potentials measured are approximately -75 mV, followed by a decrease to -84 mV until all the TPM is emulsified. At pH 10.1, the zeta potentials start slightly higher at -40 mV and show a slight increase to -21 mV after 130 min, followed by a return to its initial value. We estimate the colloidal stability to determine if droplets grow *via* coalescence (see Supporting Information Section S3 for details on the calculations). To determine the energy barrier we used a Hamaker constant of $A = 2.7 \cdot 10^{-20} J$, as an upper bound and represents the maximum value tabulated for silica particles interacting across a water medium.⁷¹ We found that at pH 10.1 all potentials measured during droplet growth lead to a stability ratio $W > 10^{20}$. This stability ratio corresponds to a droplet coalescence half-life $> 10^{22}$ seconds. Note that we make certain approximation, including ignoring possible change in ionic strength during emulsification. In reality, deprotonation of hTPM molecules can locally increase the ionic strength. Additionally, we do not consider other possible attractive interactions such as hydrogen bonding. However, based on this analysis it is unlikely that ρ is decreasing due to droplet coalescence. Therefore, we conclude that at pH 10.1 droplets grow primarily through Ostwald ripening, which leads to a decrease in the number density and an increase in droplet diameters. DLVO calculations also support the droplets being colloiddally stable at pH 11.5 but the droplet number density remains generally constant throughout the emulsification process. These observations indicate that shortly after the nucleation event further droplet growth at pH 11.5 occurs through addition of TPM species from the reservoir rather than from other droplets.

We estimate the flux of TPM species in the aqueous phase by filling a rectangular capillary with alkaline solution and then deposited TPM at the interface (**Fig. 6a**). We then measured the change in the volume of the TPM phase (dV_{TPM}/dt), where t is the time and V_{TPM} is the total volume of the oil phase, as well as the interfacial area (A_{OW}) during emulsification (**Fig. 6b**). From the change in volume and interfacial area we can estimate the molar flux (N_{TPM}) into the aqueous phase using **Eqn. 1**:

$$\frac{dV_{TPM}}{d\tau} = -N_{TPM}A_{OW}\nu \quad (1)$$

where $\nu = 2.38 \cdot 10^{-4} \text{ m}^3/\text{mol}$, the molar volume of TPM.⁷² Based on these measurements we obtain a mean average molar flux of $1.4 \cdot 10^{-4} \pm 1.3 \cdot 10^{-4} \text{ mol/m}^2\text{s}$ (**Fig. 6c**). There is some variability in the measurements, especially early on, but the flux is relatively constant throughout the emulsification process.

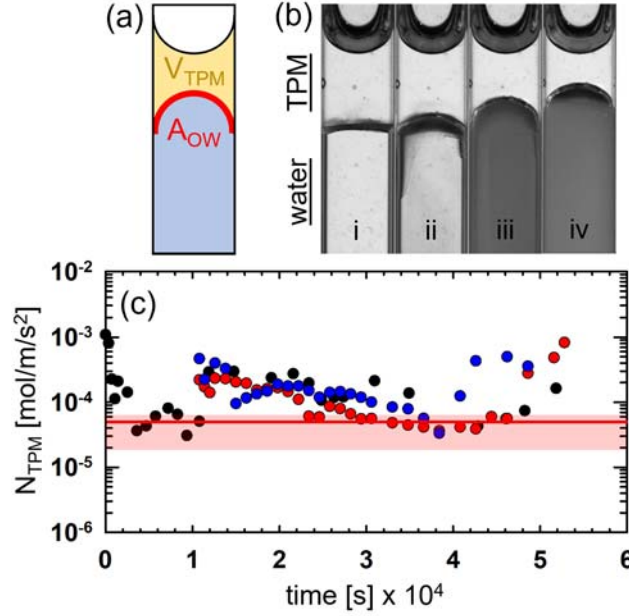


Figure 6. Droplet growth at pH 11.5 is hydrolysis-limited. (a) Schematic of cross section during TPM conversion measurements in rectangular capillary measuring TPM volume (V_{TPM}) and the interfacial area (A_{OW}). (b) Images used to determine N_{TPM} after (i) 9,000 s, (ii) 24,000 s, (iii) 34,000 s, (iv) 54,000 s. (c) Three separate measurements of N_{TPM} at pH 11.5. The red solid line indicates the molar flux determined by fitting the droplet growth data to Eqn. 2 in (Supporting Information **Fig. S6**). The shaded region indicates the error in ρ_c used to fit for the molar flux.

If the rate-limiting step for droplet growth is transfer of TPM species to the aqueous phase, a constant molar flux would lead to a cubic relationship for droplet growth (D vs t , **Fig. 5a**). The relationship arises from a volume conservation between the loss of TPM ($\frac{dV_{TPM}}{dt}$) to the total increase in the volume occupied by droplets ($\frac{dV_d}{dt}$). From this volume conservation we obtain the growth rate for the droplets:

$$-\frac{dV_{TPM}}{dt} = (\rho_c V_{aq}) \cdot \frac{\pi}{6} \frac{dD^3(t)}{dt} = \frac{dV_d}{dt} \quad (2)$$

where V_{aq} is the volume of the aqueous phase, while ρ_c is the number density taken at the plateau value in **Fig 5b** ($3.72 \cdot 10^{10} \text{ cm}^{-1}$). Eqn. 2 assumes that the solubilized TPM is distributed evenly amongst all the droplets, that the volume of the aqueous phase is constant, and that the molar volume of TPM is also constant. The second assumption is likely valid as the total volume of TPM is at most 1% of the volume of the aqueous phase. If we plot the data of **Fig. 5a** in terms of the cube of the diameter we see that the experimental data is indeed linear (Supporting Information **Fig. S6**). We calculate the corresponding N_{TPM} and compare it to the independent flux measurements (red line in **Fig. 6b**). The shaded region in **Fig. 6c** indicates the experimental error determined from the uncertainty in the number of droplets. We see that the estimated molar flux based on the droplet growth is lower, but within an order of magnitude from the measured one. Therefore, it is likely that at pH 11.5 the droplet growth rate is limited by the transport of TPM species to the aqueous phase (likely hTPM).

In summary, the induction time is significantly longer at pH 10.1 than at pH 11.5. After induction, the initial droplet diameter and growth rate is comparable at both pHs. The two growth rates diverge when at pH 10.1 the droplets grow mainly via Ostwald ripening, while the droplet growth is limited by TPM hydrolysis at pH 11.5. For both pH, the droplets are not kinetically stable and will continue to grow after all the oil is emulsified. The emulsion becomes polydisperse over time and then aggregate or completely phase separate.

Droplet nucleation and growth with stabilizing agents

Surfactants and nanoparticles can act as stabilizing agents during droplet formation and growth (**Table 1**).^{10, 28} At pH 10.1 both the initial diameter and induction times vary for different surfactants. The longest induction time is when SDS is present (ionic) and the shortest is with CTAB (cationic), while the induction time with Tween (nonionic) lie between the two and is slightly longer (but comparable) than in the absence of surfactant. In addition, in the presence of CTAB the droplets are significantly larger and are initially polydisperse ($PDI > 0.3$) but the droplets become monodisperse ($PDI = 0.067$) after emulsification, see Supporting information **Fig. S7**. The differences in induction times with surfactant charge indicate that electrostatic interactions likely play a role in droplet nucleation. This observation aligns with previous findings in a variety of material systems where charged surfactants may prevent charged monomers from adsorbing to the nuclei surface through electrostatic repulsion, therefore leading to additional droplet nucleation.⁷³⁻⁷⁵ In contrast, at pH 11.5, the presence of surfactants leads to significantly smaller droplets diameters, approximately ~15 nm with induction times that are comparable to those measured without surfactants.

The induction times when silica particles are dispersed in the aqueous phase are by far the shortest, and are similar at pH 10.1 and pH 11.5, suggesting that the particles catalyze TPM hydrolysis. The droplets also form a dense layer close to the oil-water interface, making it challenging to monitor them due to their localization (Supporting Information **Fig. S8**). The first droplets detected by DLS are at $8,400 \pm 400$ s at pH 11.5 while the emulsion turbidity appears to the naked eye at 300 ± 60 s (**Table 1**). Therefore, we also report t_{ind} as the time at which we first observe turbidity by eye in the cuvettes. The first measurement of the droplet size is 175 nm and remains nearly constant, indicating that the localization of the droplets near the interface also prevents us from capturing the growth by DLS.

We then investigate the determining factors for droplet growth in Tween solutions. The droplets follow a cubic growth (linear portion in **Fig. 7a,e**) before reaching a plateau. After a period with a high uncertainty the number of droplets remains relatively constant over time (**Fig. 7b,f**). A cubic growth along with a constant number density is consistent with a growth mechanism limited by monomer addition. Increasing the Tween concentration (pH 11.5) decreases both the droplet diameter and the growth rate (**Fig. 7e**). Therefore, the decrease in droplet size with an increase in Tween concentration is due to the nucleation of more droplets in solution as shown in **Fig. 7b,f**. In fact, if we account for the difference in the number of droplets, the overall change in emulsified TPM is constant (within uncertainty) when the concentration of Tween increases, compare dV_d/dt in **Table 2**. However, increasing the amount of oil for the same Tween concentration (squares to circles, 1 mM Tween: $\omega = 21$ to 42.), leads to larger droplets but a comparable emulsification rate. Following the same approach, we find that the emulsification rate of TPM is lower at pH 10.1 than at pH 11.5 for the same Tween concentration (dV_d/dt in **Table 2**). Combined, these observations show that (a) the Tween concentration sets the number of droplets at nucleation, (b) the amount of oil determines the final droplet diameter, and (c) the emulsification rate is constant at pH 11.5 for different Tween or oil concentrations. The emulsification rate is primarily determined by the solution pH, consistent with the importance of hydrolysis and condensation of TPM.¹⁴

Comparisons of the growth rate between SDS and Tween help understand the possible contribution from electrostatic interaction on the droplet growth (**Fig. 7**). We expect electrostatic repulsion between the ionic SDS surfactant and deprotonated hTPM molecules. As with Tween, the droplet growth with SDS is cubic (**Fig. 7a,e**). However, with SDS we observe possible additional nucleation events. At pH 11.5 there is a rapid increase in the number of droplets ~420 min after induction. At pH 10.1 the droplet number density increases continuously shortly after induction until the TPM reservoir is depleted (**Fig. 7b,f**). With SDS we also observe a plateau in the droplet diameter before the TPM reservoir is completely emulsified. For example, at pH 10.1 the droplet diameter saturates when emulsification is only 50% complete but the emulsification of the bulk TPM phase continues (**Fig. 7c**). Electrostatic repulsion may inhibit the addition

of TPM molecules to negatively charged clusters early on leading to an increase of the number of nuclei. This effect could continue throughout the emulsification and lead to additional nucleation events as more TPM are solubilized.⁷⁶⁻⁷⁷ Another possible manifestation of electrostatic repulsion between hTPM and SDS is the much smaller diameter of the droplets at induction time with SDS than with Tween (for the same molar ratio of surfactant of $\omega = 42$), see **Table 1** and **Fig. 7e**. The decrease in droplet size is due to far more (almost 100X) droplets initially present in SDS solutions.

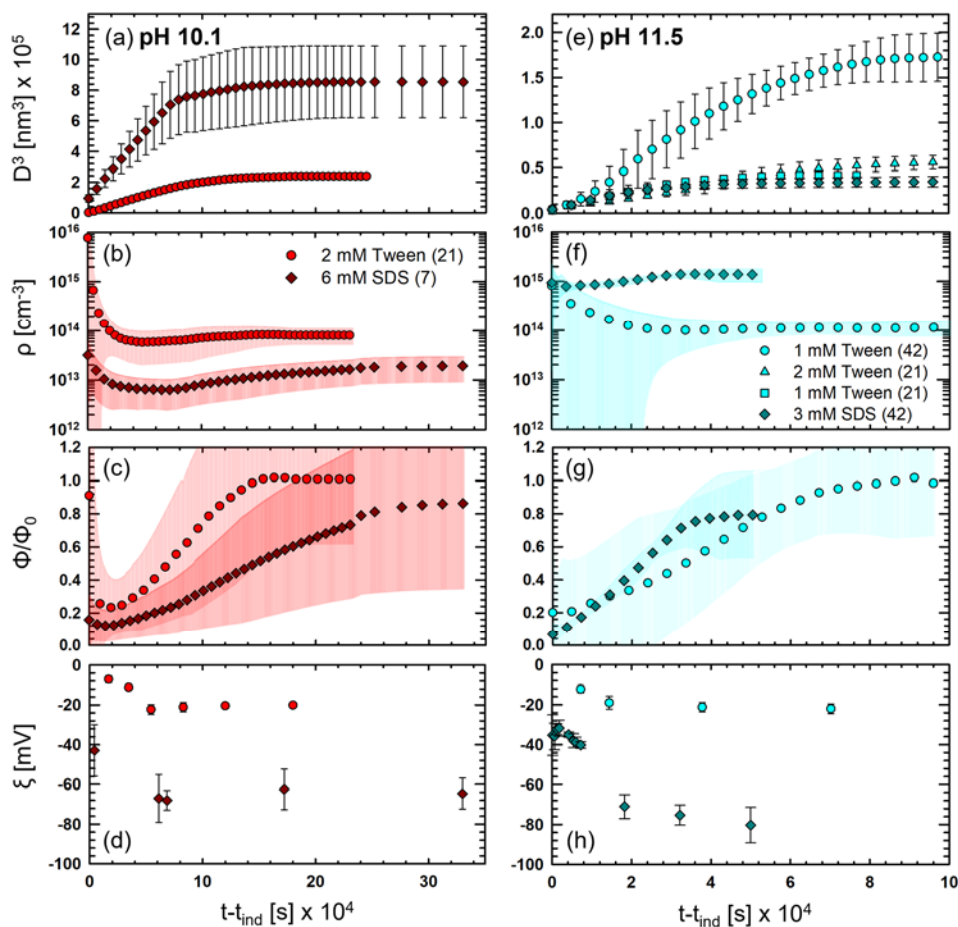


Figure 7. Droplet growth with surfactants. Left column (red) is for pH 10.1 and right column (blue) is for pH 11.5. The legends indicate the concentration of surfactant and the molar ratio (ω) of TPM to surfactant in parentheses. (a,e) Time evolution of the cubed droplet diameter during emulsification. (b,f) Number density of droplets during emulsification. The shaded regions represent the error propagated from the droplet size and turbidity measurements. (c,g) Fractional conversion of TPM as the volume fraction of the dispersed phase (Φ) over the theoretical maximum (Φ_0). (d,h) Droplet zeta-potential during emulsification, diluted into pH matching solution.

To understand the droplet growth mechanism, we first determine if surfactant-stabilized droplets are stable against aggregation. For both surfactants the zeta potential is negative and relatively constant over time (**Fig. 7d,h**). For Tween-stabilized droplets the zeta potential is $\zeta \approx -21$ mV. For SDS-stabilized

droplets the zeta potential is $\zeta \approx -40 \text{ mV}$ early in the emulsification process and becomes increasingly more negative over time. DLVO calculations show that for both surfactants the surface charge is sufficient to stabilize the droplets (see Supporting Information **Fig. S11**). Moreover, droplets stabilized with Tween remain stable when the salt concentration increases to 0.5 M (**Fig. S10**), indicating that additional steric interactions between Tween molecules also stabilize the emulsions. For SDS solutions the droplets are destabilized by an increase in salt concentration (see Supporting Information **Fig. S11**), confirming that the emulsions are electrostatically stabilized. Based on these results we determine that Tween and SDS are stable during the growth phase. Combined with the constant (or increasing) number density of droplets and the colloidal stability we rule out coalescence as a growth mechanism.

Table 2. TPM conversion calculations from droplet growth and capillary conversion experiments.

pH	Stabilizing agent	Φ_{TPM}	Conc. [mM]	$dV_d/dt^{(a)}$ [$\mu\text{L/s}$] $\times 10^4$	$N_{\text{TPM}}^{(b)}$ [mol/m ² /s]	$dV_{d-hl}/dt^{(c)}$ [$\mu\text{L/s}$] $\times 10^4$
10.1	None	0.01	--	--	$1.8 \pm 1.4 \cdot 10^{-5}$	1.7 ± 1.3
	Tween	0.01	2	0.7 ± 0.5	$2.6 \pm 1.3 \cdot 10^{-5}$	2.5 ± 1.3
	SDS	0.01	6	0.2 ± 0.1	--	--
11.5	None	0.01	--	4.9 ± 2.5	$1.4 \pm 1.3 \cdot 10^{-4}$	13 ± 1
	Tween	0.01	1	1.5 ± 0.4	$8.3 \pm 4.0 \cdot 10^{-5}$	8 ± 4
	Tween	0.01	2	1.2 ± 0.2	--	--
	Tween	0.005	1	1.2 ± 0.4	$8.3 \pm 4.0 \cdot 10^{-5}$	8 ± 4
	SDS	0.03	3	4.9 ± 0.7	--	--
	Silica	0.01	3 wt %	--	$3.0 \pm 4.0 \cdot 10^{-3}$	340 ± 230

^aDetermined from droplet growth data, Eqn. 2

^bMeasured from volume conversion experiments

^cCalculated using N_{TPM} and constant A_{OW} of TPM drop at the air-water interface (39 mm²)

We investigate if the droplet growth rate is hydrolysis limited in Tween solutions. We measured the flux of TPM into the aqueous phase using imaging in capillary vials (shown in **Fig. 2**). The molar flux of TPM (N_{TPM}) is nearly constant over time and increases with pH (**Fig. 8** and **Table 2**). When comparing with the same measurements in the absence of surfactant we find that Tween leads to a decrease in the molar flux (at a given pH), see N_{TPM} in **Table 2**. The adsorption of Tween at the oil-water interface could decrease the hydrolysis rate of TPM or inhibit condensation reactions at the droplet interface.⁷⁸ We then compare the measured molar flux from imaging the capillaries to the one calculated from Eqn. 2 using the number density of droplets and their diameters obtained from turbidity and DLS. At both pHs, the fluxes determined from the droplet growth curves (lines in **Fig. 8a**) are comparable but consistently lower than the values measured from imaging (data points in **Fig. 8a**). The discrepancy between the measured molar flux and the one obtained from the droplet growth could stem from a number of simplifying assumptions in our analysis. First, we assume a constant interfacial area between the TPM-aqueous interface during emulsification, but we observe a decrease in the interfacial area as the TPM is depleted. We also assumed that the solubilized TPM species are uniformly distributed into all the droplets in solution, and neglect possible concentration gradient (of droplets and TPM species). Nevertheless, the discrepancy in the measured fluxes is larger than in the absence of surfactant (**Fig. 6c**). These results suggest that Tween hinders the incorporation of TPM into existing droplets, perhaps through the formation of micelles or through additional energy barriers at the oil-water interface.

Finally, we are unable to monitor the growth of droplets using DLS or turbidity formed in silica particle dispersions due to the localization of the droplet near the interface. However, we measured the TPM solubilization through imaging. We observe a significantly larger TPM conversion when silica nanoparticles are present (**Fig. 8b**). These findings support the hypothesis that silica nanoparticles catalyze TPM hydrolysis to promote transfer of TPM to the aqueous phase and emulsification.

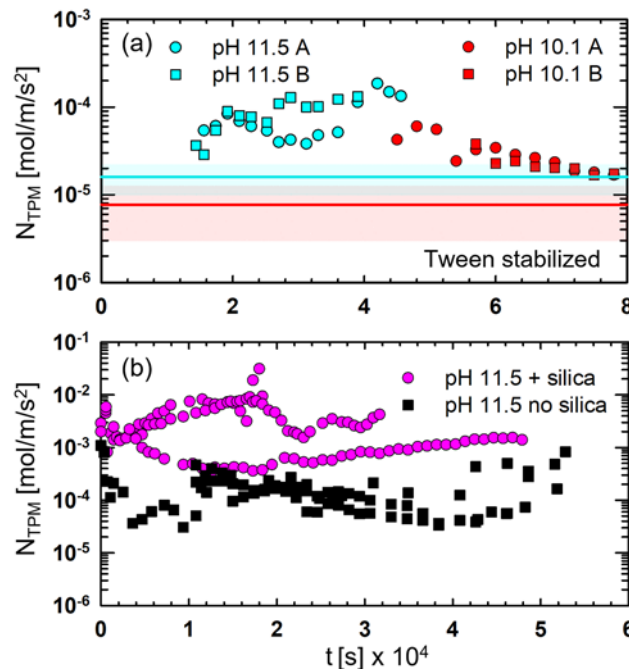


Figure 8. TPM flux with surfactants and nanoparticles in solution. The molar flux determined from direct measurements of TPM conversion for (a) pH 10.1 2 mM Tween and pH 11.5 1 mM Tween for two trials (A,B) and (b) pH 11.5 with (purple circles) and without (black squares) silica nanoparticles. The red and cyan horizontal lines represent the molar flux determined by fitting the data from Fig. 7a,e to Eqn. 2.

5. Conclusions

In this study, we investigated the droplet formation and growth process during the spontaneous emulsification of TPM. In particular, we studied the role of diffusion and solubilization of TPM species under quiescent conditions in the presence and absence of external stabilizing agents. Our findings can be summarized as follows.

- In the absence of stirring the mechanisms of diffusion and stranding likely drives the emulsification of TPM (**Figs 2-4**).
- In the absence of surfactant at pH 10.1 droplets grow primarily through Ostwald Ripening (**Fig. 5**). At pH 11.5, the droplets primarily grow through addition of TPM to a set of primary droplets (**Fig. 5**), and the rate-limiting step is TPM hydrolysis (**Fig. 6c**). At both pHs the emulsions are unstable at long times in the absence of surfactants.
- The presence of surfactants leads to sub-100 nm stable droplets. Tween droplets are sterically and electrostatically stabilized. SDS droplets are electrostatically stabilized (**Fig. 7e,h**). The decrease in droplet size in the presence of surfactants is associated with an increase in the number of droplets in solution (**Fig. 7 b,f**).

- Tween-stabilized droplets grow through addition of TPM species to the primary droplet distribution, similar to the surfactant-free case (**Fig. 7**) but the rate-limiting step might not be TPM hydrolysis (**Fig. 8a**). The pH and surfactant concentration set the number of droplets, while the oil volume fraction sets the final droplet diameter. Electrostatic interactions between SDS and TPM species affect the nucleation and growth process. Data shows evidence of additional (or continuous) nucleation events and a much larger number of droplets in solutions (**Fig. 7b,f**).
- Silica particles act as a catalyst for TPM hydrolysis (**Tables 1-2, Fig 8b**).

In summary diffusion and stranding sets limitations on the composition of oil mixtures that can be emulsified with TPM. Alternatively, the need for partial miscibility in the aqueous phase could be leveraged for separation applications. We have shown previously how the presence of stabilizing agents can be used to create TPM nanoparticles with a precise control over their diameter, and our work here can help refine and understand these protocols. In particular, surfactants may be used to create monodispersed TPM droplets at lower pH where pure TPM droplets are polydisperse ($< \text{pH } 10$). Finally, we also see that emulsification in the presence of silica nanoparticles is significantly more complex due to the catalytic nature of the particles at the oil-water interface, which warrants further investigation.

Supporting Information

Supporting information is available free of charge. Interfacial tension data; Analysis combining dynamic light scattering and turbidity; DLVO calculations, droplet growth (cubic) at pH 11.5; and Droplet growth with surfactant or nanoparticles.

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TOC Figure

