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Sprouting droplets driven by physical effects alone

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Abstract

Combining a partially miscible three liquid system with interfacially trapped silica colloids, we show that small droplets can exhibit dramatic growth phenomena driven by physical effects alone. The mass dense droplets sprout tubes which grow vertically upwards in a gravitational field and respond to the presence of other droplets in their path. Two of the liquids in our system are water and toluene. By varying the third liquid we are able to relate the growth behavior to the details of the underlying three fluid phase diagram and the changes to the interfacial tension. Additionally, we introduce a pendant drop in the path of our growing drop. We use this to confirm that growth is driven by the partitioning of solvents, that exchange of solvents between droplets is chemically selective and that the exchange behavior can itself generate further growth phenomena.

Introduction

There is great current interest in making liquid droplets in a host solvent responsive and functional.[1] This includes having droplets follow a concentration gradient around a maze,[2] respond to light[3,4] or self-replicate.[5] As part of this, particle-stabilized interfaces have been harnessed as a model membrane which simultaneously stabilizes the interface between the two liquids and allows transport across it.[6] Here, the particles are on the colloidal scale; they become trapped at a liquid-liquid interface if they exhibit partial wettability with both liquids.[7] The trapping tends to be extremely strong, however, there remain meso-scale interstices which readily permit diffusion between the two phases. Aqueous droplets stabilized by silica nanoparticles have been used to support in vitro gene expression of enhanced green fluorescent protein and to improve the activity of a range of enzymes.[8] The growth and division of particle-stabilized droplets has been demonstrated, driven by the synthesis of methanol within an aqueous droplet. The methanol leads to the rupture of the membrane and the formation of a new particle-stabilized interface.[9] The complex behavior of droplets observed under these conditions is also indicative of the range of phenomena which could occur in the most demanding industrial uses of emulsions.

Life-like growth in liquid-liquid systems can also be observed in “chemical gardens” where the interfacial layer is synthesized in situ.[10] Chemical gardens are the intriguing life-like tendrils which grow when a seed crystal of a metal salt is immersed in an aqueous solution of sodium silicate (or other source of anions).[11–13] The metal ions enter solution and react, forming a semipermeable colloidal membrane around the seed crystal. Tendril growth is then driven by the osmotic pressure associated with water crossing the membrane.[14] Recent research has modeled the growth modes of the tendrils and how interacting tendrils compete for resources.[15] Chemical garden-like phenomena do not always involve an interface which is synthesized in situ: ice brinicles are brine-rich tubes growing beneath sea ice which typically have interfaces stabilized by lipids produced by phytoplankton.[16] Their growth direction is downwards, driven by the mass density of the brine solution.

We recently reported the millimeter-scale sprouting of particle-stabilized water droplets injected into a bath of toluene and ethanol.[17] Vertical sprouting was found to be due to the ethanol in the immediate vicinity of the injected drop preferentially partitioning into the sessile water droplet. The ethanol then rises up to the top of the droplet due to its buoyancy (relative to water), locally reducing the interfacial tension at the top of the droplet, which then directs the sprouting. New particles from the bath are adsorbed onto the freshly exposed liquid-liquid interface. The stability of the growing drop at all times was assumed to be dependent on the balance between gravity and interfacial tension. Noticeable sprouting was observed only at certain intermediate concentrations of ethanol and silica particles. After prolonged growth the drop eventually buckles under its own weight due to the internal phase being more dense than the surrounding solvent. This system differs very significantly from almost all of those described above in that it relies solely on physical partitioning and not on chemical synthesis within the droplet or at its interface.

In the phenomena reported here and for several other important droplet instabilities, any elasticity that the interface may exhibit can have a controlling influence. For example, we discovered the sprouting droplets by combining the well-known Marangoni instability[18] (see also[19,20]) with interfaces made elastic by a layer of adsorbed particles.[17] The interfacial particles suppress the dancing of a pendant drop, but on longer time scales a $50\,\mu\ell$ droplet grows a centimeter in ten minutes. An alternative case is Ostwald ripening: a population of droplets of different sizes tend to coarsen as the dispersed phase moves from smaller to larger droplets. Here elastic interfaces can be used to suppress the movement of the dispersed phase hence preventing droplets from changing size.[21,22] By contrast, an interfacial layer of particles is unable to suppress compositional ripening (exchange between droplets driven by different chemical contents).[23] The experiments we report here, in which we use two droplets with different contents, are a stylized study of compositional ripening. Being able to understand and control the ripening behavior of these systems would be valuable for the production of stable emulsions encapsulating varied chemical contents (so-called compound emulsions).

In this Article we demonstrate the cause of droplet sprouting by exploring variations in the behavior in response to a range of experimental conditions. We assess the sprouting behavior for four different solvents and then relate the results to the underlying three-fluid phase diagrams. We next show how the sprouting droplets respond to a pendant droplet in their path. This enables us to demonstrate that the advancing droplet requires a bath of alcohol to continue to grow. Finally we reveal new phenomena that occur when the sprouting droplet makes contact with the pendant droplet; this includes the building of a colloidal bridge and controlled exchange of solutes.

Results and discussion

To begin, we observe that using methanol in the bath instead of ethanol (used previously[17]) can also induce droplet sprouting (see Figure 1). The parameters which could change when we change the solute include the rate of partitioning into the droplet, the final equilibrium compositions, the interfacial tension between the two phases and the particle interactions. All of these factors are also dependent on the volume fraction of alcohol used. Here we typically use a $50\,\mu$L droplet of deionized water in $5\,$mL of bath solution containing toluene, $0.2\,$vol% fumed silica and various concentrations of the solutes.[1001] In a further series of experiments we introduce an additional pendant droplet so as to further probe how the sprouting droplet interacts with its environment.

[1001] For a particle-stabilized water droplet in a bath of toluene with methanol, the growing behavior continues for several hours. Increasing numbers of particle-stabilized tubes sprout for the first hour. This ultimately results in the formation of a large particle-stabilized neck. Subsequently there is fluid flow leading to the droplet arriving at the top of the sample.

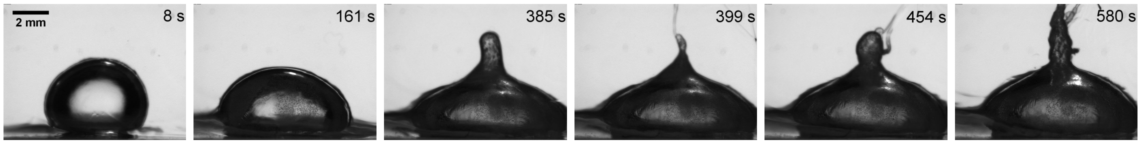

Figure 1: A series of frames showing the behavior of a water droplet in a bath of 0.2 vol% fumed silica, 25 vol% methanol and toluene as a function of time.

The role of different solutes on the growth behavior

Pure solutes

Sprouting droplet experiments[17] can be illustrated using the equilibrium phase diagram of the liquid components, e.g. Figure 2(a). The water droplet corresponds to the right hand vertex of the triangle while the bath has a composition which is a specific location along the left-hand edge. The growth emerges in the presence of particles as this system attempts to reach thermodynamic equilibrium via partitioning of the solvents. We find that a sessile water droplet in a bath of toluene, fumed silica particles and methanol also displays sprouting behavior (see Figures 1 and 2(b)). This growth is, however, not as uniform as for a water droplet in a toluene bath with ethanol. Initially, the water droplet expands and collapses in a series of rapid movements which initially occur approximately every 10 s, but subsequently more slowly. These differences are likely to stem from the underlying phase behavior: the tie lines on the ternary phase diagram of toluene, water and methanol have a steep gradient indicating that, at equilibrium, the majority of the methanol is in the water rich phase, see Figure 2(b). This reflects the much stronger affinity methanol has for water in comparison to toluene; hence, a large volume of methanol partitions into the water droplet quite rapidly. In addition, the droplets in this system do not sprout a stable, smooth tube but rather overspill with the liquid from the droplet streaming upwards; this stream slowly becomes particle-stabilized. Using methanol as the solute rather than ethanol requires a larger volume fraction of solute in the system before any sprouting behavior is observed (this may relate to the interfacial tension, see below).

In contrast, a sessile water droplet in a bath of toluene, fumed silica particles and 1-

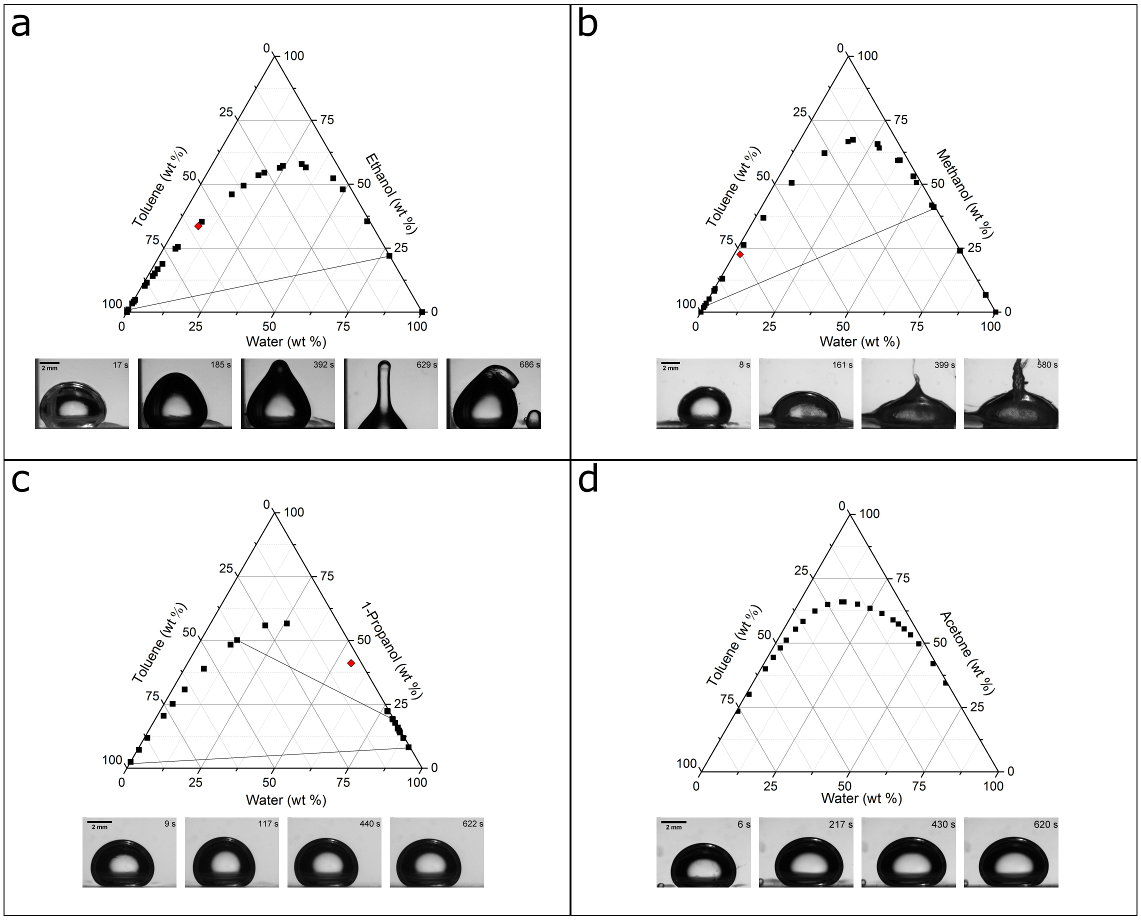

Figure 2: Ternary phase diagram showing the regions of miscibility and immiscibility for various three fluid systems; below each are frames showing the time dependent behavior of a particle-stabilized water droplet. The red diamond marks the critical point and the line represents a typical tie line. **a**: Toluene-Water-Ethanol. Images show a sprouting water droplet in a bath of 15 vol% ethanol in toluene. **b**: Toluene-Water-Methanol. Images show a sprouting water droplet in a bath of 25 vol% methanol in toluene. **c**: Toluene-Water-1-Propanol. Images show a slightly expanding water droplet in a bath of 10 vol% 1-propanol in toluene. **d**: Toluene-Water-Acetone. Images show a slightly expanding water droplet in a bath of 25 vol% acetone in toluene.

propanol did not display any sprouting behavior, see Figure 2(c). Instead the droplet simply expanded slightly in size. This behavior was observed for all the volume fractions of 1-propanol used, although there was a change in shape of the droplet from spherical to ellipsoidal as the concentration was increased. In comparison to ethanol and methanol there will be much less 1-propanol partitioning into the water droplet because it is much more evenly divided between the two phases. We suggest that there is not enough alcohol partitioning into the droplet to cause the increase in volume required for tube sprouting behavior. [1002]

The solute acetone, similar to 1-propanol, in a bath with toluene and fumed silica did not cause any sprouting behavior in a sessile water droplet (see Figure 2(d)). Instead, the water droplet expanded slightly in size and this is, again, likely to be due to insufficient quantities of solute partitioning into the droplet . Indeed, the tie lines for the ternary system of water, toluene and acetone indicate that the majority of the acetone will be found in the toluene-rich phase.[24]

Interfacial tension measurements

The pendant drop method was used to measure the interfacial tension between the equilibrium compositions of the water-rich and toluene-rich phases given an initial binary concentration of the alcohols methanol, ethanol and 1-propanol in toluene.[25] The interfacial tension between water and toluene was found to be $35.2 \pm 0.1\,\mathrm{mN/m}$ which is within 5% of the literature value at 20 °C.[26] Increasing the volume fraction of any of the alcohols moves the system closer to the critical point on the phase diagram, leading to a decrease in the interfacial tension, see Figure 3.

Methanol, which decreases the interfacial tension least, has a much stronger affinity for the water-rich phase than the toluene-rich phase, meaning that the majority of the methanol is found in the water-rich phase, see Figure 2(b). By contrast, 1-propanol, which decreases the interfacial tension most, does not display such a strong preference; consequently, it is more evenly split between the two phases, see Figure 2(c), which makes the phases more similar at lower volume fractions. A high interfacial tension can mean that the particle-laden interface is too rigid,[27] hence, for methanol, sprouting was only observed at high alcohol concentration. A low interfacial tension can mean that gravity controls the shape of the droplet, hence the change in droplet shape for 1-propanol with increasing alcohol

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[1002] In principle, the lack of sprouting behavior could be because this is a cross system: the slope of the tie lines changes sign, Figure 2(c). However, the volume fractions of 1-propanol used in these experiments were lower than the crossing point.

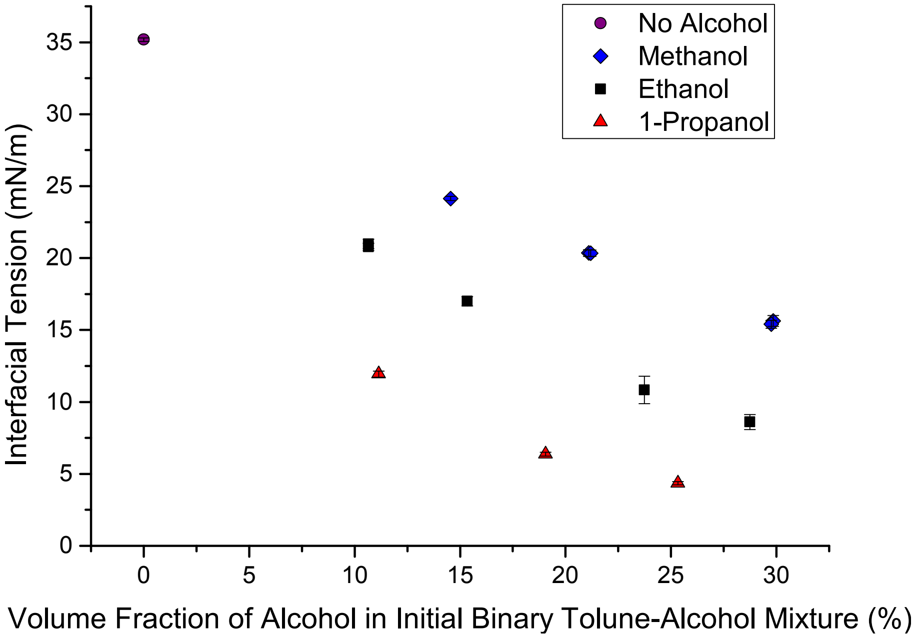

Figure 3: A graph showing the interfacial tension values as measured using a pendant drop tensiometer for equilibrium compositions containing different alcohols compared to the initial volume fraction of alcohol in a binary mixture with toluene. These values are found using the conditions and constituents as for the growth behavior experiments

concentration.

Mixtures of alcohols

To observe how the growth phenomenon changes for subtle variations in interfacial tension and partitioning behavior we have used mixtures of alcohols. The samples were characterized by the volume fraction of alcohol in the bath and the effective carbon length (a 1:1 mixture of ethanol and methanol would produce an effective carbon chain length of 1.5). The systems were then grouped on a diagram according to the observed behavior and Figure 4 shows seven different regions.

Region 1 extends across all volume fractions of alcohol at high effective carbon chain length and also down to intermediate effective chain length at low alcohol volume fractions (see Figure 4). Here the droplet simply expands in a similar way to the pure 1-propanol case. For these compositions there is not enough alcohol partitioning into the droplet and the large range of interfacial tension values included indicates that a soft interface will not

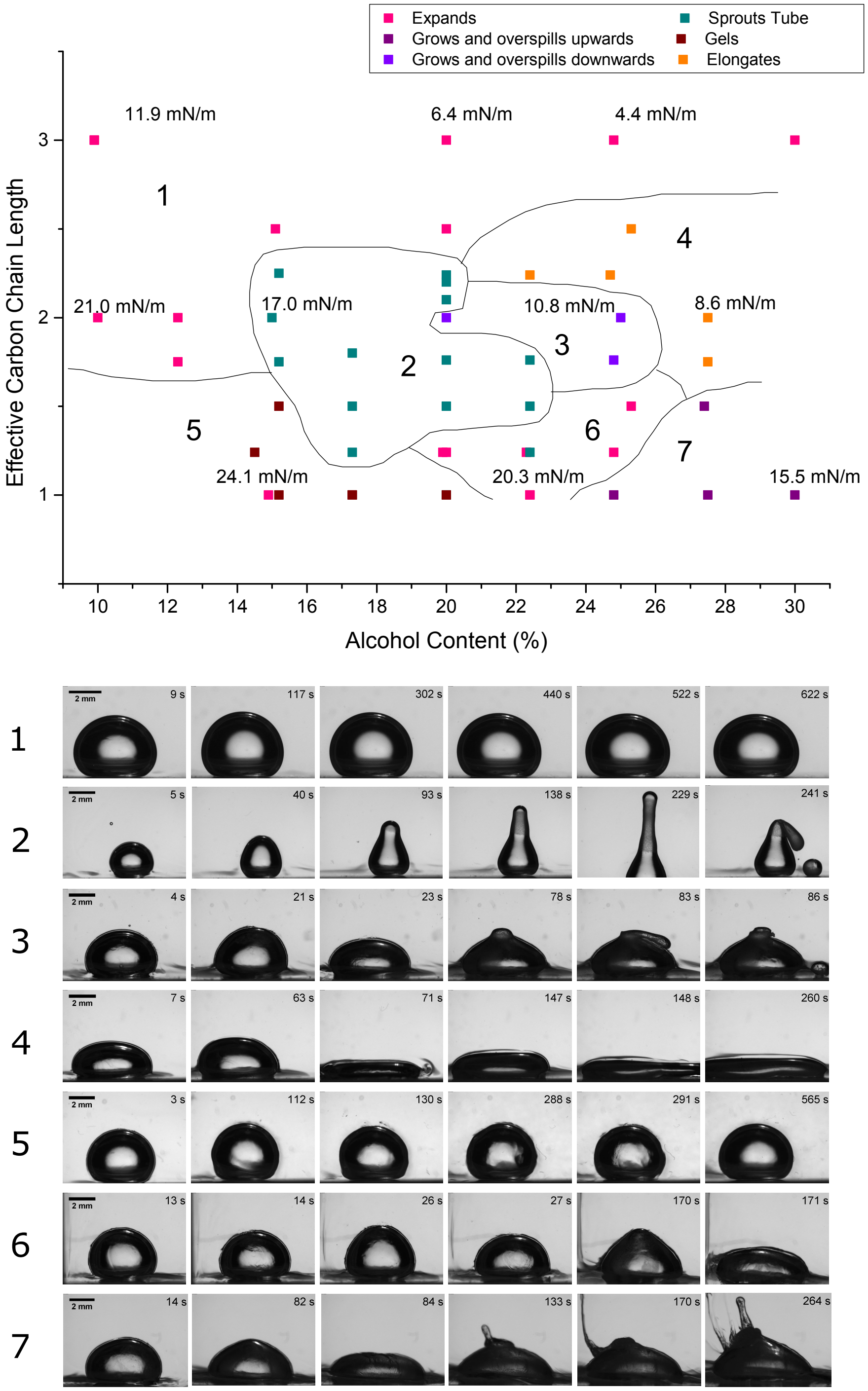

Figure 4: A diagram showing the changes in water droplet behavior depending on the effective carbon chain length and the initial alcohol content of the toluene phase. The solid lines are indicative of possible boundaries between regions. The interfacial tension at specific points is also given on the diagram. Example time series of droplet behavior in each numbered region are included (note the variations in time scales).

yield growth on its own.

Region 2 is at intermediate effective carbon chain length and intermediate alcohol content; here sprouting behavior is observed. There is significant partitioning and intermediate interfacial tension: the interface is not too rigid to allow growth and not so low that the interface is too soft to support growth.[17]

Region 3 is at slightly higher alcohol content than region 2 but still at intermediate effective carbon chain length. In this region, sprouting behavior is observed but now the droplet appears to erupt with the tube overspilling down the side of the original droplet (see Figure 4, image sequence 3). Evidently, the interface is failing to provide a rigid support for growth or a barrier to the internal phase due to either the lower interfacial tension, the change in wettability of the particles or both.

Region 4 is at high alcohol content and intermediate effective carbon chain length. The droplets in this region were observed to expand, collapse, elongate and roll around the base of the cuvette. This behavior is reminiscent of that of a sessile droplet with no interfacial particles[17] and follows from substantial partitioning of alcohol combined with a soft or uncovered interface.

Region 5 is where the particle-particle interactions become important and the bath was observed to become very viscous, even gel-like. This is at low effective carbon chain length and low alcohol content (see Figure 4). Here, droplet growth is impeded by a surrounding particle network.

Region 6 is characterized by higher alcohol content and low effective carbon chain length; the behavior changes again with the droplet expanding, attempting to sprout a tube and then collapsing repeatedly. This is indicative of a high rate of alcohol partitioning that is still insufficient to overcome an interface which is too rigid.

Region 7 initially shows droplet behavior like region 6 with rapid growth and collapsing cycles; subsequently, an upward liquid stream is observed to burst from the droplet which then becomes particle stabilized (see Figure 4, image sequence 7). This behavior is observed for systems with low effective carbon chain length and high alcohol content and has partly been described in the pure methanol solute Section above. The large volume of alcohol partitioning into the droplet in this region is sufficient to overcome the rigid interface.

Quantitatively, sprouting results when a large volume expansion (associated with a tie line slope at least as steep as from ≈ pure toluene to 3:1 water:alcohol) is combined with an interfacial tension in the range 9-18 mN/m.

Mass transfer between two droplets

Behavior of a sprouting droplet in the vicinity of a pendant droplet

In this Section we look at how the mass transfer, using ethanol as the solute, can be altered locally by introducing a pendant droplet of pure water into the path of a sprouting droplet. Two different outcomes are observed depending on when the pendant drop is created (see Figure 5(a, b)). If the pendant drop is injected at approximately the same time as the sessile one, Figure 5(a), the ethanol partitions into both droplets at about the same rate. This leads to the formation of a layer depleted of ethanol along the water-oil interface in the region surrounding the pendant drop. Due to the existence of this 'halo' around the pendant drop, the sessile water droplet continues its growth towards regions that are more abundant in ethanol, i.e. it grows around the boundary of the pendant droplet, Figure 5(a). Conversely, if the pendant drop is formed once the sessile one has started sprouting and is approaching the needle, then it is appropriate to assume that ethanol from the bath has only been depleted extremely close to the pendant drop, hence the sprouting droplet can approach (see Figure 5(b)). This contrasting behavior underlines the fact that the growth is driven by the partitioning of the ethanol.

When a pendant droplet is created as the sprouting droplet approaches, the two liquid-liquid interfaces never actually meet (see Figure 5(b)). At a small separation distance (≈2 mm) a dark cone is observed to grow downwards from the pendant droplet. This structure makes contact between the two droplets. We assume that the formation of the cone

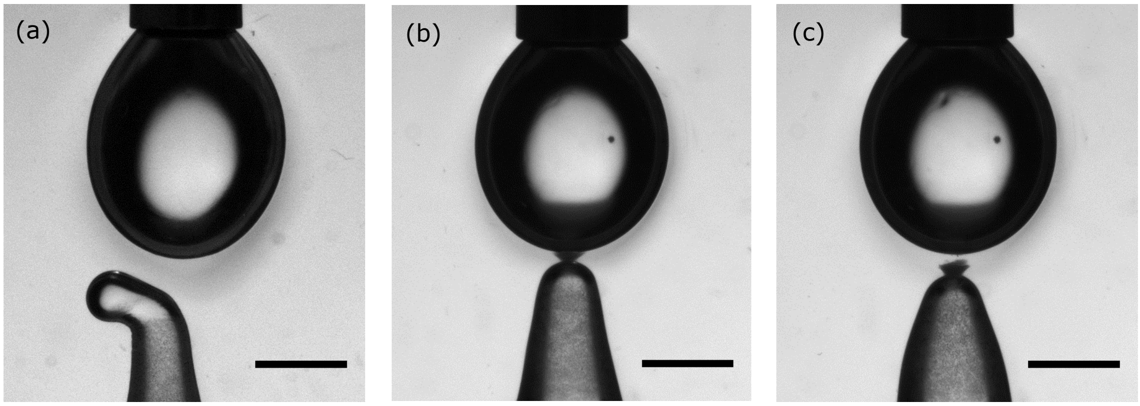

Figure 5: **a**: The behavior of a pendant drop of water and a sessile drop of water created simultaneously in a bath of 0.49 vol% fumed silica, 20 vol% ethanol and toluene. **b**: The behavior of a pendant drop of water and a sessile drop of water where the pendant drop was created after the sessile drop had started sprouting in a bath of 0.49 vol% fumed silica, 20 vol% ethanol and toluene. **c**: One minute later, the bridge pictured in **b**, detaches from the pendant droplet. The scale bars are 1.5 mm.

is driven by the diffusion of water from the pendant droplet, which is water only slightly enriched with ethanol, to the growing droplet, which is significantly enriched in ethanol. The transfer process is a form of compositional ripening. The presence of water in the continuous phase has destabilized the hydrophobic particles and caused them to aggregate. About a minute after the formation of this colloidal cone, it detaches from the pendant droplet due to being pulled down by its own weight (see Figure 5(c)). The cone retains its shape, confirming that it has self assembled from solid particles aggregated into close proximity.

Mass transfer between pairs of sprouting and pendant droplets

There is evidence from Figure 5(b) that water is transferred from a fresh pendant droplet to a sessile droplet which grows close to its interface. To determine whether large scale solvent transfer will happen in response to any composition difference, we have included sodium bromate in the aqueous pendant droplet and ferroin indicator solution and sulphuric acid in the sessile droplet with water,[28,29] see Methods. As with Figure 5(b) above, the sessile droplet is created earlier and so is enriched in ethanol compared to the pendant droplet. If the reactants meet in significant quantities a color change from red to blue should be observed. The two droplets were pushed into contact and held that way for a prolonged period (see Figure 6). The red color of the sessile droplet is a strong and stable feature of the system for at least half an hour. Color change does not occur until the two droplets eventually coalesce (see Figure 6(e)).

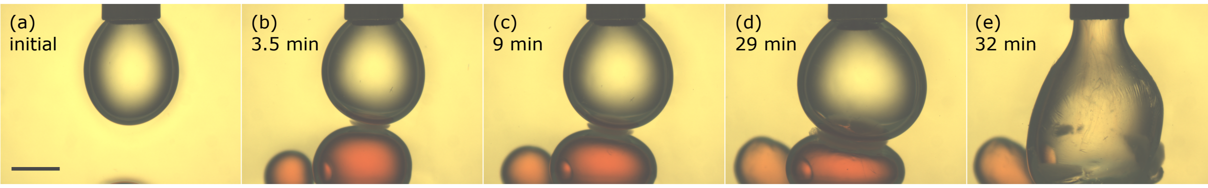

Figure 6: **a-e**: A sequence of frames showing pendant and sessile drops pushed into close contact. The droplets contain the separate reactants (see text); the sessile droplet is created earlier and so is enriched in ethanol compared to the pendant droplet. Water is transferred from the pendant droplet to the sessile droplet, the reactants are not. A second sessile droplet sits to one side and plays no significant role in the experiment. **e**: After being pushed into contact for a prolonged period the two droplets coalesce and the reaction takes place, resulting in a transparent droplet. Across the sequence of frames there is a slight increase in the volume of the pendant drop due to further mixture descending from the reservoir above. The scale bar is 1.5 mm.

In the frames shown in Figure 6(b-d) colloidal aggregation is evident from the cloudy region surrounding the point of contact between the droplets. We associate this with water moving through the oil phase and destabilizing the dispersed particles. Our results strongly suggest that, while water does move between droplets, the small molecule reactants are confined to one droplet or the other. Hence the higher concentration of ethanol in the sessile droplet is the biggest driver of solvent transfer; by contrast, the other reactants have negligible influence.

Conclusions

Particle-stabilized interfaces have previously been employed as a design motif in life-like droplets. Here we have demonstrated how they can be used in droplets which sprout and grow. The growth is driven by alcohol partitioning into the water droplet which causes an increase in volume and tends to lower the interfacial tension near the top of the droplet. We have shown that in order for sprouting behavior to occur, a fine balance between the volume of alcohol partitioning into the droplet and the value of the interfacial tension between the two phases is necessary. If the interfacial tension is too high and the volume of alcohol too low then no growth behavior is observed. If the interfacial tension is too low and the volume of alcohol too high then any attempt at growth results in collapse. Sprouting results when a large volume expansion (associated with a tie line slope at least as steep as from $\approx$ pure toluene to 3:1 water:alcohol) is combined with an interfacial tension in the range 9-18 mN/m. These features can be controlled via the choice of alcohol and liquid proportions. By placing a pendant drop in the path of the sprouting droplet we have been able to confirm both that the sprouting drop needs an environment rich in alcohol to grow and that a fresh pendant droplet will lose water via diffusion to the growing droplet. We have gone on to demonstrate that the alcohol concentration is the dominating driver of diffusion from one droplet to another, swamping any influence of other reactants. This effective selectivity means that we have complete control based on the phase diagram and the elasticity of the interfaces.

The formation of the particle cone between droplets of different composition (Fig. 5b) is a previously unreported feature of compositional ripening. The control of such phenomena is of crucial importance for complex delivery applications, for example, in the agrochemical sector. Here it is necessary to create emulsions which are robust if the farmer chooses to mix them with a second emulsion-based product. Understanding the instabilities of mixed-droplet systems is a crucial step towards developing the stable emulsions required. Separately, the sprouting growth mode we observe (Fig. 2a) is curiously life-like. It is fascinating that this behavior is not limited by our reliance on physical effects. Growth is driven by partitioning and the growing droplet is stabilized by building blocks (particles) which it acquires from the surroundings. It seems to us that, because interfacial particles confer elastic properties to the interface while allowing transport across it, they are an important design motif for future studies of mechanics, growth and transport in many kinds of tubular structures.

Experimental

Materials

The solvents toluene (Analytical Reagent grade, Fisher), methanol (Analytical Reagent grade, Fisher), 1-propanol (anhydrous 99.7%, Sigma Aldrich), acetone (GPR RECTAPUR, VWR), absolute ethanol (AnalaR NORMAPUR, VWR) and sulfuric acid (95-97%, Sigma-Aldrich) were used as received. Distilled water was filtered and deionized with a Milli-Q system to a resistivity of 18.2 $\mathrm{M\Omega\,cm}$. Fumed silica particles (HDK H30), size ≈100 nm, were a gift from Wacker-Chemie (Burghausen). Sodium bromate (99%, Sigma-Aldrich) and ferroin indicator (0.025 M, Fluka) were used as received.

Methods

Growth behavior

Firstly, the relevant mass of fumed silica particles was weighed out to give 0.2 % particle volume fraction. Next 10 mL of toluene was added to the vial followed by the appropriate volume of acetone, ethanol, methanol or 1-propanol to give the required volume fraction of solute. This mixture was then dispersed using the ultrasonic probe (Sonics Vibracell VCX500) for two minutes using a 30 s on, 30 s off cycle at 20% amplitude. The square cuvette on a Krüss EasyDrop tensiometer (model 65 FM40Mk2) was used to hold the bath liquid at a volume of ≈5 mL. Typically, a ≈50 μL droplet of deionized water was then injected into the bath directly after video recording was started in order to view the growth behavior at room temperature. The behavior of the droplet was recorded over a period of approximately ten minutes.

Interfacial tension

The method by Joos was followed in order to find the volume fraction of alcohol in a binary mixture with toluene for a tie line of a given equilibrium composition.[25] The relevant equilibrium compositions for the binary mixtures used in the growth experiments were then made up by combining toluene, alcohol and water. The mixtures were vortex mixed for 20 s in order to ensure the system is homogeneous. The density of both the water and toluene phases was measured using a density meter (Anton Paar, DMA 4500). Each phase was measured three times and the mean density used as an input value for measuring the interfacial tension. Interfacial tension measurements were made using the pendant drop method on the tensiometer which includes software to analyze the drop shape. The largest possible pendant drop of the denser water phase was injected into a bath of 5 mL of the toluene phase by a supported Hamilton syringe. The shape was measured every 30 s at room temperature over a period of twenty minutes to check that the interfacial tension was stable. This experiment was then repeated 2-3 times, with fresh liquids and the mean taken to be the interfacial tension.

Mass transfer experiments

Small batch (10 mL) samples were prepared by mixing 10-30 vol% ethanol and 0.1-0.6 vol% H30 hydrophobic silica particles in toluene solvent. The resulting mixture was then ultrasonicated as described in the Growth behavior Section above. The water droplets (5-40 μL) were then injected into the bath using a Hamilton syringe either manually or using the syringe pump on the tensiometer. Videos of sprouting sessile drops and turbulent pendant drops were recorded for 3000 frames at a rate of 6 fps and were subsequently analyzed qualitatively.

For the reactant transfer experiments, the bath liquid was prepared and dispersed as above, with 20 vol% ethanol and 0.2 vol% H30 hydrophobic silica particles. The aqueous phase used for the pendant droplet contained 0.3 M of sodium bromate and the aqueous phase used for the sessile droplet contained 0.3 M sulfuric acid and 1.7 mM of ferroin indicator. A QImaging MicroPublisher 3.3 RTV color camera was used to record the videos of droplets containing dye.

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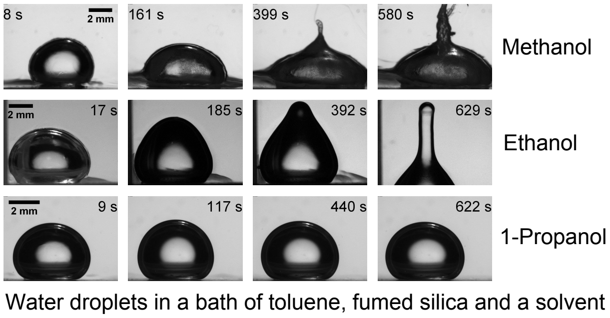

Figure 7: Graphical Table of Content