

“Self-Shaping” of Multicomponent Drops

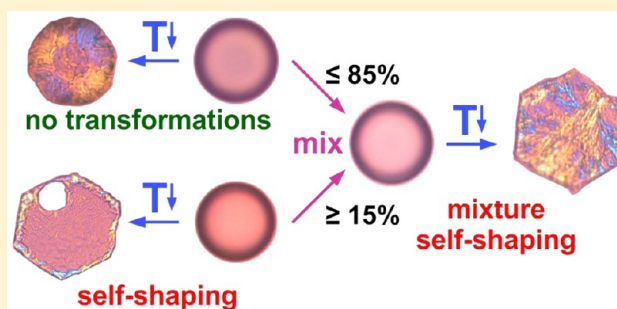
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S Supporting Information

ABSTRACT: In our recent study we showed that single-component emulsion drops, stabilized by proper surfactants, can spontaneously break symmetry and transform into various polygonal shapes during cooling [Denzkov et al. *Nature* 2015, 528, 392–395]. This process involves the formation of a plastic rotator phase of self-assembled oil molecules beneath the drop surface. The plastic phase spontaneously forms a frame of plastic rods at the oil drop perimeter which supports the polygonal shapes. However, most of the common substances used in industry appear as mixtures of molecules rather than pure substances. Here we present a systematic study of the ability of multicomponent emulsion drops to deform upon cooling. The observed trends can be summarized as follows: (1) The general drop-shape evolution for multicomponent drops during cooling is the same as with single-component drops; however, some additional shapes are observed. (2) Preservation of the particle shape upon freezing is possible for alkane mixtures with chain length difference $\Delta n \leq 4$; for greater Δn , phase separation within the droplet is observed. (3) Multicomponent particles prepared from alkanes with $\Delta n \leq 4$ plastify upon cooling due to the formation of a bulk rotator phase within the particles. (4) If a compound, which cannot induce self-shaping when pure, is mixed with a certain amount of a compound which induces self-shaping, then drops prepared from this mixture can also self-shape upon cooling. (5) Self-emulsification phenomena are also observed for multicomponent drops. In addition to the three recently reported mechanisms of self-emulsification [Tcholakova et al. *Nat. Commun.* 2017 (8), 15012], a new (fourth) mechanism is observed upon freezing for alkane mixtures with $\Delta n > 4$. It involves disintegration of the particles due to a phase separation of alkanes upon freezing.



■ INTRODUCTION

In our recent studies,^{1–4} we showed that micrometer size emulsion drops of single chemical substances such as *n*-alkanes, alkenes, alcohols, triglycerides, etc., can change their shape upon cooling. Depending on the surfactant and oil components in the system, spontaneous transformations start at a temperature a few degrees above or below the bulk melting temperature of the emulsified oil. Subsequently, drops pass through several stages in a common shape sequence—from fluid polyhedra, various flat platelets such as hexagonal, tetragonal, and trigonal prisms, and, finally, they transform into thin fibers.

These deformations are triggered by freezing of the surfactant adsorption layer before the bulk of the droplet, upon which a plastic rotator phase of self-assembled oil molecules, with long-range translation order, is formed next to the drop surface. This plastic phase spontaneously forms a frame of plastic rods at the drop perimeter which supports the polygonal structure and could, finally, transform into plastic fibers extruded from the drop surface. Simple energy arguments^{1,4,5} showed that the formation of this plastic phase can provide the energy gain needed to overcome the increasing

surface energy of the deforming droplets. This concept was developed into a detailed theoretical model⁵ which explained the observed sequence of platelet shapes and their statistics in qualitative agreement with experiments. The model analyzed also the evolution of protrusions (fibers) and some other phenomena observed experimentally.

The new self-shaping phenomenon is important in two contexts because it provides (1) new method for synthesis of particles with various complex shapes and (2) system of very simple composition which exhibits the basic processes of morphogenesis.

However, in nature (as waxes and biological membranes) as well as in consumer products that we use every day (i.e., lipsticks, cosmetic creams, etc.) alkanes are usually found as mixtures with various chain lengths. In cosmetics, e.g. “vaseline” is a mixture of alkanes with lengths between 14 and 50 carbon atoms. Therefore, it is of both practical and scientific interest to

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study the self-shaping phenomena in multicomponent emulsions.

Crystallization of alkanes and their mixtures is widely studied in the literature.^{6–20} It is known that the odd n -alkanes with chain lengths between 13 and 41 carbon atoms (C atoms) crystallize into an orthorhombic crystalline lattice, while the even chain-length alkanes with between 14 and 26 C atoms crystallize into a triclinic crystalline lattice.⁶ However, upon cooling, before reaching the thermodynamically stable crystalline structure, alkanes pass through intermediate phases known as rotator phases. Rotator phases are fluid phases in which molecules do have long-range positional order with respect to their translational degree of freedom, but the order is missing with respect to their rotational degree of freedom. Rotator phases have been observed for alkanes with chain length between 12 and 50 C atoms in bulk,^{6–9} emulsion drops,^{10–12} and microcapsules.^{13–17}

Typically, binary alkane mixtures exhibit a single crystalline phase if the length of the longer alkane is up to 22% longer than the length of the shorter alkane in the mixture (i.e., difference in the chain length of up to 4 C atoms for alkanes with chain length up to 20 C atoms).¹⁸ Otherwise, upon cooling, a phase separation within the solid phase is observed. As with the single alkanes, rotator phases have been observed as intermediate phases also for alkane mixtures. It has been shown that chain mixing increases the temperature range of stability of the rotator phases.^{13–17,19}

Mondieig et al.²⁰ studied the phase diagrams of various binary mixtures for alkanes of consecutive chain lengths ($\Delta n = 1$) and mixtures with $\Delta n = 2$.²⁰ Briefly, upon cooling, an alkane mixture goes from a liquid state to a two-phase region where liquid and rotator phases coexist. Further cooling leads to transformation into either a rotator or a crystalline phase depending on the ratio between the alkanes in the mixtures. If a rotator phase is formed, it transforms into a stable crystalline phase at a lower temperature. A schematic phase diagram presenting the main regions observed in the binary alkane mixtures is shown in Figure 1. For shorter alkanes ($n \leq 20$), the

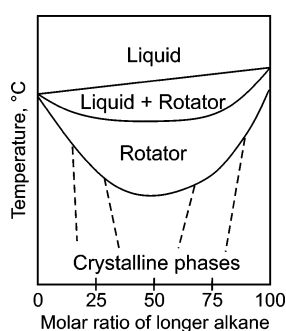


Figure 1. General schematic phase diagram for two-component alkane mixtures.

rotator phase is R_1 —a lamellar structure with the alkane molecules stacked perpendicularly to the lamellar planes and being able to rotate around their long axis. It has a bilayer stacking sequence ABAB.

In the current study, we present the main features of the self-shaping phenomena as observed with multicomponent drops. Consecutively, we describe the processes observed upon cooling, freezing, and melting of these drops and how they differ from the corresponding processes observed with single-

component drops. We comment on the influence of the expanded area of stability of the rotator phases in multicomponent mixtures on the drop self-shaping phenomena.

EXPERIMENTAL SECTION

Materials. As a dispersed phase in most of the emulsions studied we used mixtures of n -alkanes (abbreviated as C_n) with different chain lengths n varied between 10 (decane) and 20 (eicosane). All alkanes were purchased from Sigma-Aldrich and have purity >99%. The melting temperatures of these paraffins are between -30 and 37 °C. The alkanes were used as received.

In another series of experiments we used 1-heptadecene, 1-eicosene, 1-decanol, 1-dodecanol, 1-tetradecanol, 1,2,3-trihexadecylglyceride (tripalmitin), and pentadecylcyclohexane. We studied also emulsions prepared with commercial oil products such as cocoa butter, lard, and coconut oil (purchased from a grocery store in Bulgaria, used without further purification), which are mixtures of molecules. Detailed information for the compounds and their relevant physical properties is presented in the Supporting Information Tables S1 and S2.

As emulsifiers we used two different series of water-soluble nonionic surfactants with the commercial names Brij and Tween (all products of Sigma-Aldrich). The Brij surfactants are polyoxyethylene alkyl ethers, C_nEO_{20} , and the Tween surfactants polyoxyethylene sorbitan monoalkylates, $C_nSorbEO_{20}$ with n varying between 16 and 18; for detailed information see Table S3. All emulsifiers were used without further purification. Their concentration in the aqueous phase was fixed at 1.5 wt %. This concentration was chosen to be sufficiently high, well above the critical micelle concentrations, to suppress the drop-drop coalescence and the surfactant depletion due to adsorption on the increased surface of the deforming drops during the experiments.

All aqueous solutions were prepared with deionized water (with resistivity >18 M Ω -cm) which was purified by the Elix 3 module (Millipore, USA).

Methods. Oil Mixtures. The alkane mixtures were prepared by mixing two or more alkanes (in a liquid state) in a certain volume ratio. Various binary mixtures of chain lengths C_{n1} and C_{n2} with Δn between 1 (two consecutive chain-length alkanes) and 10 (decane + eicosane) were studied. We also studied some ternary mixtures of alkanes and a seven-component mixture. The alkane volume ratio was varied between 10 and 90% for the longer alkane in the mixtures. Emulsions of a single alkane were also studied (i.e., volume ratio corresponding to 0 or 100% in the mixture) for comparison of the observed trends.

To check whether the same processes are observed with mixtures of compounds from different homologous series (for example, alkane + alcohol or alkane + alkene, etc.), we prepared various mixtures in 1:1 volume ratio. We also studied various mixtures of non-self-shaping substances (substances which cannot induce self-shaping when the emulsion drops are prepared only with them) mixed in different ratios with self-shaping substances.

Emulsion Preparation. All emulsions were prepared by membrane emulsification, in which drops with relatively narrow size distribution were generated.^{21–24} The polydispersity indices of the prepared emulsions by both number and volume, σ_X , were always $\sigma_X \leq 1.1$. The polydispersity is defined as the ratio $\sigma_X = d_{X84}/d_{X50}$, where “X” is “N” (when the values are calculated by number) or “V” (when calculated by volume). The d_{X50} diameter represents the mean drop diameter, while d_{X84} represents the diameter for which 84% of the drops have drop sizes smaller than the given diameter (when calculated by number) and 84% of the dispersed oil is contained in drops with diameters smaller than the given diameter (when calculated by volume).

The oily phase was emulsified by passing it through the pores of the glass membrane under pressure, into the continuous phase (aqueous surfactant solution). We used a laboratory Microkit membrane emulsification module from Shirasu Porous Glass Technology (SPG, Miyazaki, Japan), working with tubular glass membranes of outer diameter 10 mm and working area of approximately 3 cm². We used

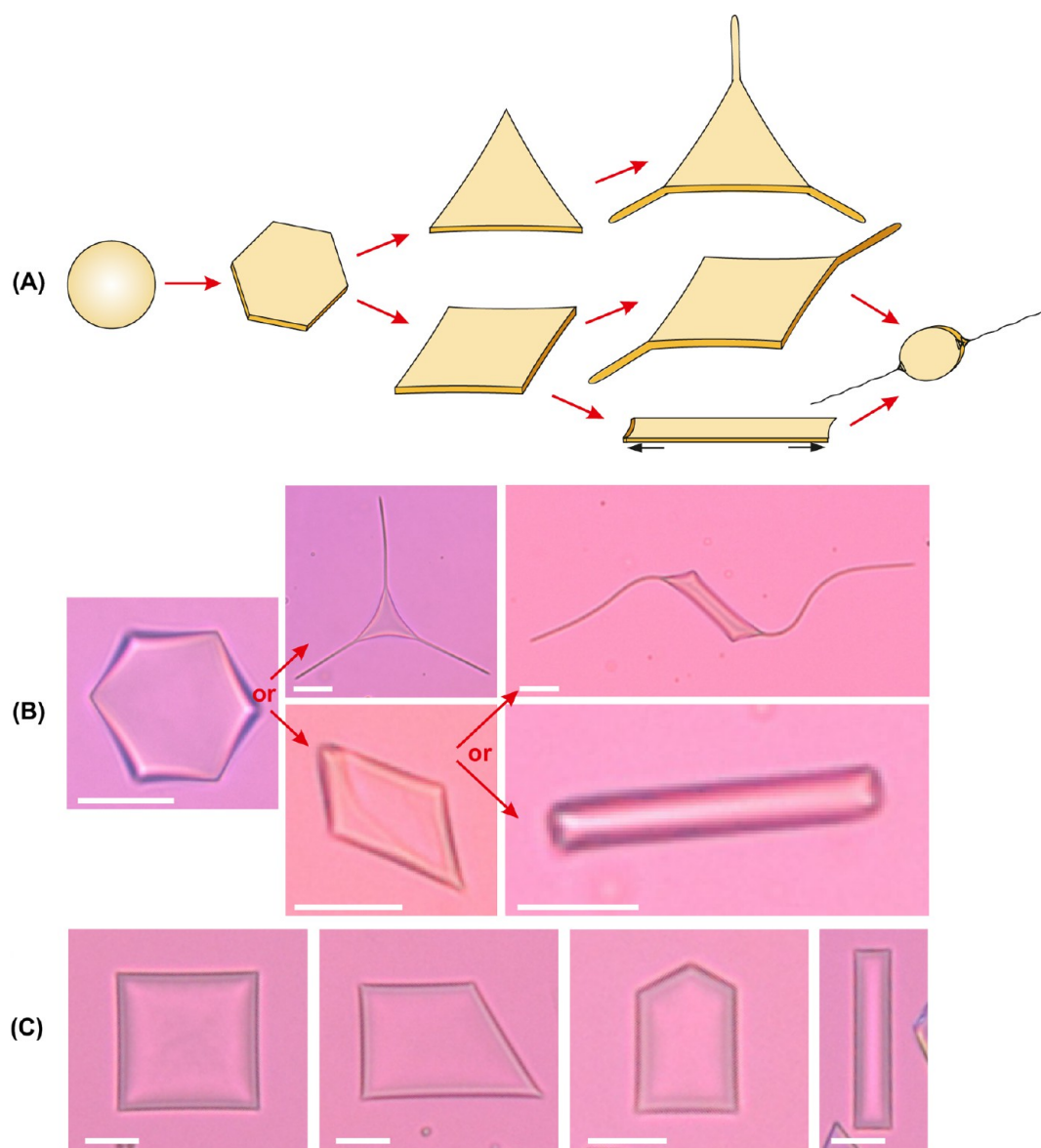


Figure 2. Drop shape transformations observed upon cooling. (A) Main stages of the drop shape evolution, observed for single- and multicomponent droplets. (B) Fluid nonspherical shapes observed with multicomponent drops of $C_{14}:C_{16} = 1:1$ v/v, stabilized by $C_{16}EO_{20}$ surfactant, initial drop diameter $\approx 17 \mu\text{m}$. (C) Fluid shapes with 90° angles, observed with multicomponent drops ($C_{16}:C_{19} = 1:1$ v/v, $C_{18}\text{SorbEO}_{20}$, $d_{\text{ini}} \approx 17 \mu\text{m}$, cooling rate 0.18 K/min). Scale bars: $20 \mu\text{m}$.

membranes with mean pore diameter of 1, 2, 3, 5, and $10 \mu\text{m}$ to prepare monodisperse droplets with mean diameters around 3, 6, 10, 17, and $32 \mu\text{m}$, respectively.

The membrane emulsification technique was used to study the behavior of a large number of similar in size drops under equivalent experimental conditions. In preliminary experiments we studied also polydisperse emulsions, prepared by simple hand-shaking or by rotor-stator homogenization of the oil–surfactant mixtures. Similar results were obtained with the drops in these polydisperse emulsions.

Optical Observation of the Drop Shape Transformations. For microscope observations, a specimen of the studied emulsion was placed in a rectangular capillary with length of 50 mm, width of 1 mm, and height of 0.1 mm. The capillary was enclosed within a custom-made metal cooling chamber, with optical windows for microscope observation (see Figure S1). The chamber temperature was controlled by a cryo-thermostat (JULABO CF30, cryo-compact circulator). The temperature in the sample during the experiment was measured using a calibrated thermocouple probe with an accuracy of $\pm 0.2^\circ\text{C}$. The thermoprobe was inserted in one of the orifices of the aluminum

thermostatting chamber and mounted in the position, where a capillary with the emulsion sample would be normally placed for microscope observations. In the neighboring orifice the actual capillary with the emulsion sample was placed. The correct measurement of the temperature was ensured by calibrating the thermocouple with a precise mercury thermometer in the respective range of temperatures measured. Also, for single alkane experiments we always observe melting of the frozen particles at temperatures very close to the known value of T_m ($\pm 0.2^\circ\text{C}$), where T_m is the literature reported melting temperature of the bulk oil.

All optical observations were performed with Axioplan and Axiomager.M2m microscopes (Zeiss, Germany). We used transmitted, cross-polarized white light, with included λ plate (compensator plate) situated after the sample and before the analyzer, at 45° with respect to both the analyzer and the polarizer. Under these conditions the liquid background and the fluid objects have typical magenta color, whereas the birefringent areas appear brighter and may have intense colors.^{25,26} When taking images for determination of the drop size

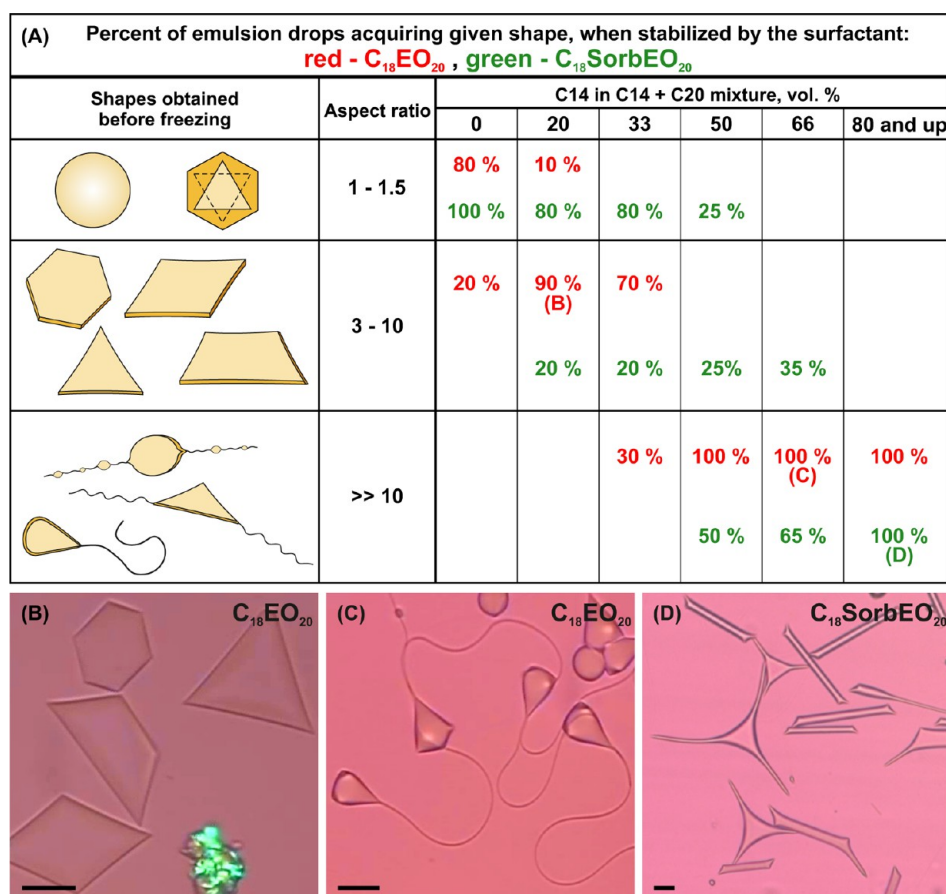


Figure 3. Aspect ratio dependence on alkane volume ratio in the mixture. For alkane mixtures, drops containing higher percentage of the short-chain component reach bigger aspect ratio before freezing. This tendency is demonstrated for two series of emulsions stabilized by two different surfactants: $C_{18}EO_{20}$ (numbers in red) and $C_{18}SorbEO_{20}$ (numbers in green). Alkane mixture $C_{14} + C_{20}$ in different volume ratios, $d_{mi} \approx 17 \pm 2 \mu\text{m}$, and cooling rate, $\approx 0.45 \text{ K/min}$. (A) Shape statistics. (B, C) Shapes obtained upon cooling of emulsion drops stabilized by $C_{18}EO_{20}$ surfactant, oil mixture with 20 and 66 vol % of C_{14} , respectively. (D) $C_{18}SorbEO_{20}$, 80 vol % C_{14} . Scale bars: $20 \mu\text{m}$.

distribution we used transmitted light. Long-focus objectives $\times 20$, $\times 50$, and $\times 100$ were used.

Freeze–Thaw Experiments. The freeze–thaw (F/T) experiments of the dispersed drops was performed as follows: (1) The cooling process started at a temperature which was 5° higher than the bulk melting temperature of the compound with highest T_m in the studied mixture (see Tables S1 and S2). The samples were cooled at a fixed cooling rate, varied between 0.15 and 1.5 K/min. The temperature in the system was lowered until complete freezing of the dispersed oil drops was observed (except for the experiment with decane where we were unable to freeze the drops entirely). Note that only the dispersed phase underwent phase transitions during our experiments and solidified. The continuous medium (aqueous surfactant solution) remained always liquid. (2) The drop melting process was performed at a fixed heating rate, $2 \pm 0.3 \text{ K/min}$. The temperature in the system was increased until reaching the melting temperature of the longer alkane in the mixture, so all of the dispersed entities were in a liquid state.

Drop Deformations. To quantify the extent of final drop deformation reached along the cooling process, we used the drop aspect ratio, defined as follows: As a reference drop size we used the diameter of the initial spherical drop. As final “drop length” we measured the longest length of the observed two-dimensional (2D) projection of the drop just before its final freezing (see Figure S2 for illustration).

Determination of the Drop Size Distribution in Emulsions. The drop size distribution in the studied emulsions was determined from microscope images. Drop diameters were determined using two procedures. For some of the experiments we measured the diameter of

the drops one by one, using custom-made image analysis software. The diameters of more than 1000 droplets were measured by this procedure. For other experiments, the drop diameter was measured using the Image Analysis Module of Axio Vision Software. More than 15 000 droplets were measured in each sample when this analysis was used. Results from the two methods were in a good agreement with each other.

The mean volume-surface diameter was determined from the relation $d_{32} = \sum_i N_i d_i^3 / \sum_i N_i d_i^2$, where N_i is the number of drops with diameter d_i .

RESULTS AND DISCUSSION

In this section we present our results for the drop self-shaping phenomena with mixtures and their comparison to the previous observations with single compounds.^{1–4} First we describe the behavior of the multicomponent drops upon cooling (transformations, freezing) and then upon heating (melting). Then we discuss the self-emulsification phenomena for alkane mixtures.

Transformations upon Cooling. In our recent publications^{1–4} we showed that droplets from substances that exhibit rotator phase transitions self-shape into a variety of polygonal shapes upon cooling (see Figure 2A). This phenomenon was observed with alkanes, alkenes, alcohols, triglycerides, and asymmetric alkanes.² It was found that no matter the substance, the droplets always follow the same evolutionary scheme—the spherical drops spontaneously change their shape, forming first

polyhedrons, which gradually flatten into hexagonal platelets and further evolve either into tetragonal platelets (parallelograms) or into triangular platelets (equilateral triangle). The last stages of the evolutionary process involve growing of protrusions from the acute angles of the platelets, and also for the tetragonal ones—a capillary instability process in which the bulk of the alkane in the shaped droplet re-forms into an ellipsoidal drop with several very sharp tips from which thin fibers are extruded.

In the current study, we found that this evolutionary scheme is followed also by all droplets containing two (or more) mixed substances that we studied. Upon cooling, the multicomponent drops pass through the exact same path of shape evolution. We did not observe any influence of the alkane chain length difference, Δn , in the mixture on the obtained nonspherical shapes upon cooling, although we varied Δn between 1 and 10 carbon atoms. Experimental pictures of multicomponent droplets with variety of shapes are shown in Figure 2B.

The condition for observation of the self-shaping process for multicomponent alkane drops is that the longer alkane in the mixture should be with no more than three C atoms longer than the length of the hydrophobic tail of the surfactant, used to stabilize the emulsion. Shorter alkanes in the mixture could be of any length. To prove this conclusion, we tested the emulsion of the binary mixture $C_{10}:C_{20} = 1:2$ (volume ratio of the alkanes in the mixture, $\Delta n = 10$), stabilized by the surfactant $C_{18}EO_{20}$. Even for this system we do observe transformations upon cooling.

Interestingly, until now we have always observed platelets with angles of 60° or 120° . However, for multicomponent droplets many platelets with 90° angles are also formed (see Figure 2C). It was found that 90° angles are most often observed for mixtures of alkanes with chain length difference ≤ 4 and for the highest cooling rate which still allows drops to self-shape. To clarify the reason for the frequent formation of 90° angles at the platelet corners, we need structural information about the molecular self-assembly within the plastic phase in the deformed droplets and particles. Such information is not available at the moment. Therefore, we could only speculate that the contact zones of the self-assembled molecular structures (plastic rods at the drop edges) have preferred angles of orientation which depend on the internal molecular structure of the self-assembled regions. This molecular structure could be different for the single-component and multicomponent droplets, resulting in different preferred angles of the platelet corners.

As with single-component drops,² drop shape evolution upon cooling is affected by the initial drop size, cooling rate, surfactant used for emulsion stabilization, and the alkane volume ratio in the mixture. Again, we observed that the smaller multicomponent drops, cooled at slower cooling rates, evolve up to further stages of the evolutionary scheme upon cooling, thus reaching bigger aspect ratios.

To study the effect of the alkane volume ratio in the mixture, we performed systematic experiments with various volume ratios for a mixture of tetradecane (C_{14}) and eicosane (C_{20}). We found that for a given surfactant, drops with larger amount of the shorter alkane reach further stages of the evolutionary scheme, while drops with larger amount of the longer alkane freeze at earlier stages. This effect is demonstrated in Figure 3 for the surfactants $C_{18}EO_{20}$ and $C_{18}SorbEO_{20}$ and drops with initial diameter $d_{\text{ini}} \approx 17 \pm 2 \mu\text{m}$. As seen from Figure 3A, when C_{20} drops are stabilized by $C_{18}EO_{20}$ surfactant, and cooled at

cooling rate 0.45 K/min, only 10% of the drops evolve up to the platelet stage. This is easily understood because the alkane in this case is with longer chain length than the chain length of the surfactant tail; therefore, the transformations are quite difficult for these drops. When only 20 vol % of C_{14} alkane is added into the oily phase, then almost all of the drops evolve up to the platelet stage (Figure 3B). If the C_{14} and C_{20} alkanes are mixed in equal volume ratios, then all drops evolve, reaching the final stages of the evolutionary scheme, as shown in Figure 3C.

The type of surfactant also plays an important role in the process, as already demonstrated in our previous study.² With surfactants containing a sorbitan ring as compared to ones without one in their hydrophilic head, it is more difficult to induce transformations under otherwise equivalent conditions (cooling rate, initial drop size, type of freezing oil). We have speculated² that the main reason for this difference is the different packing of the surfactant adsorption layer, resulting in different thickness of the rotator phases formed near the drop surface.

We observe that surfactants allowing easier transformations with single alkane also allow easier transformations for droplets of alkane mixtures. For example, as seen in Figure 3A, all drops of $C_{14}:C_{20} = 1:1$ v/v stabilized by $C_{18}EO_{20}$ reach the final stage of the evolutionary process, while this happens only at a much greater volume ratio with respect to tetradecane, $C_{14}:C_{20} = 4:1$ for drops stabilized by $C_{18}SorbEO_{20}$ (Figure 3D).

Plastification and Freezing. After the drops exhibit transformations in their shape, upon further cooling they undergo a final phase transition in which the fluid nonspherical particles transform into frozen (plastified) nonspherical particles. In this section, we describe in more details the peculiarities related to this final phase transition in mixed systems.

Upon cooling of single-component drops, for compounds where shape transformations are possible, we observed² up to three consecutive phase transitions: $L \rightarrow R_{\text{CI}} + L \rightarrow R_{\text{CV}} + L \rightarrow S$. The transition $L \rightarrow R_{\text{CI}} + L$ occurs during the transformation from an isotropic liquid drop (L) to a nonspherical liquid particle ($R_{\text{CI}} + L$), which may also exhibit a capillary instability, after which very thin fibers are formed ($R_{\text{CV}} + L$), and a final phase transition when complete freezing of one of the previous states into a solid crystal is observed (S).²

However, it has been shown²⁰ that in alkane mixtures with $\Delta n = 1-2$, below the region of the coexistence of rotator and liquid phases, there is a wide temperature range in which only rotator phase is observed prior to the formation of the stable crystalline phase (see Figure 1 and Figures 2 and 3 from ref 20). Mondieig et al.²⁰ report the existence of the rotator phase (before the final transition into a stable crystalline phase) down to -20 to -30°C for binary mixtures of alkanes with chain length less than 20 C atoms.²⁰ For that reason, the expected final phase transition in our experiments with multicomponent mixed drops is $R_{\text{CX}} + L \rightarrow R_{\text{CX}}$ (a process of plastification) instead of the formation of crystalline solid phase S (see Figure 1). Here, R_{CX} denotes any rotator phase formed in the micrometer-sized drops. For most multicomponent drops, exactly this expected sequence of phase transformations was observed.

However, we observed an additional step in the emulsions stabilized by C_nEO_{20} and alkanes with chain lengths similar to the number of carbon atoms in the surfactant tail; the extruded threads undergo a plastification phase transition before the

plastification of the main body of the deformed particle (see Figure 4 for illustration). Typically, when long threads are

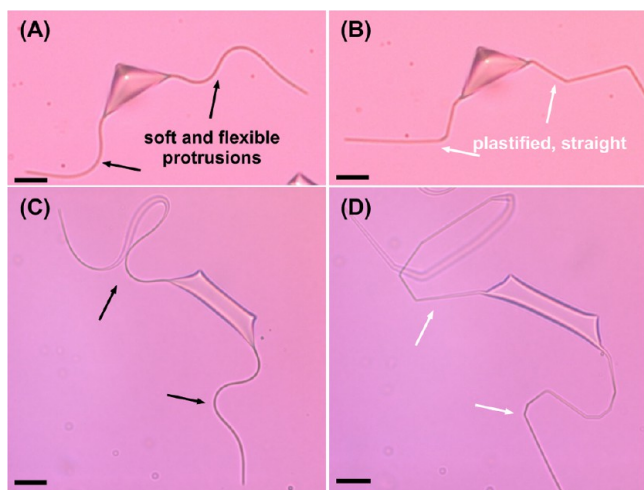


Figure 4. Plastification of extruded fibers. *n*-Alkane mixture drops from tetradecane and hexadecane (volume ratio 1:1), stabilized by $C_{16}EO_{20}$ undergo a phase transition not observed with single-component drops. Upon cooling, drops change their shape and start to extrude soft and flexible protrusions (A) and (C); however, at a certain temperature, below T_d but above the plastification temperature, the protrusions suddenly become straight and stiff (B) and (D). Scale bars: 20 μm .

extruded, they are soft, flexible, and easily bent. Similar threads are also observed in the initial stages of the evolutionary process of mixed $C_{14}:C_{16} = 1:1$ drops, stabilized by $C_{16}EO_{20}$ surfactant (see Figure 4A,C). However, when a certain temperature is reached, a phase transition only within the protrusions is observed; they suddenly become straight with some defects along their length, seen as sharp angular changes of thread direction (Figure 4B,D). After this phase transition, the fibers do not grow more or change upon further cooling, which confirms that they have been plastified before the plastification of the main body of the deformed fluid particle. A similar process is observed for the emulsion of $C_{16}:C_{18} = 1:1$, stabilized by the surfactant $C_{18}EO_{20}$. In the latter case, the temperature at which the phase transition is observed is much closer to the temperature of plastification of the main body of the deformed particle, so the separate plastification of the fibers is not so easy to distinguish.

The final phase transition, $R_{CX} + L \rightarrow R_{CX}$ (or S in the case of single-component drops), is easily detectable with an optical microscope in polarized light because of the visible changes in the particle color. Before the final phase transition, the fluid particles do not have intense colors because the rotator phase at their periphery is with thickness around several dozens to several hundred nanometers.^{1,2} The colors appear when the rotator/crystalline structure is formed within the whole particle because of the birefringence of the thicker ordered domains of the plastified/frozen particle.

The single-component frozen particles have bright saturated colors and grained appearance which reflects their polycrystalline (domain) internal structure (see Figure 5A). Multicomponent plastified particles which are formed from alkanes with chain length differences up to four C atoms, look very different (see Figure 5B–F). These particles do preserve their shape after the final freezing, but they appear much more homogeneous in structure. Also, the observed colors are very

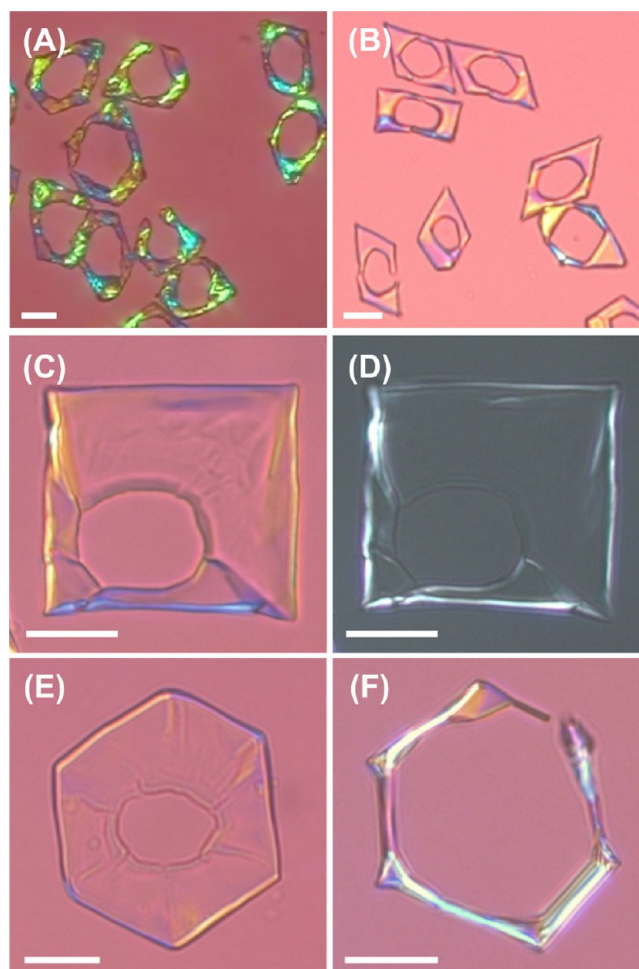


Figure 5. Plastification of multicomponent drops with $\Delta n \leq 4$. The alkanes are (A) C_{16} , (B–E) $C_{16}:C_{18} = 1:1$ v/v, and (F) $C_{16}:C_{17} = 1:1$ v/v. All emulsions are stabilized by the surfactant $C_{18}SorbEO_{20}$. (A) The frozen single-component particles have bright intense colors and “grainy” structure. (B) The tetragonal bicomponent particles look very different from the single-component particles. They have only faint colors and look much more homogeneous in structure. (C, E) Multicomponent particles have bright intense colors only at their edges, while their interior is almost transparent because the particles are filled with rotator phase, rather than with a crystalline phase. This hypothesis is confirmed by image (D) showing the same square particle as in (C) but with λ -plate being placed at 90° with respect to the polarizer and analyzer, instead at 45° as in all other pictures. (F) For some of the frozen particles bright, single-color rods are well visible at the particle periphery. Scale bars: 20 μm .

different from those observed with the single-component particles; most of the particles are almost transparent, showing bright colors only at their edges (see Figure 5B,C,E). Also, while we observe mostly green and blue colors with single-component particles, the multicomponent particles are mainly blue and yellow. Figure 5D shows the same particle as Figure 5C but with λ (compensator) plate placed at 90° with respect to the polarizer and analyzer, instead at 45° as in the rest of the pictures (i.e., the same as in cross-polarized light without compensator plate). Bright parts are observed only at the particle periphery, where the colors are in Figure 5C, confirming that only the molecules at the particle periphery are very well ordered, while the rest of the particle is in a more disordered rotator phase.

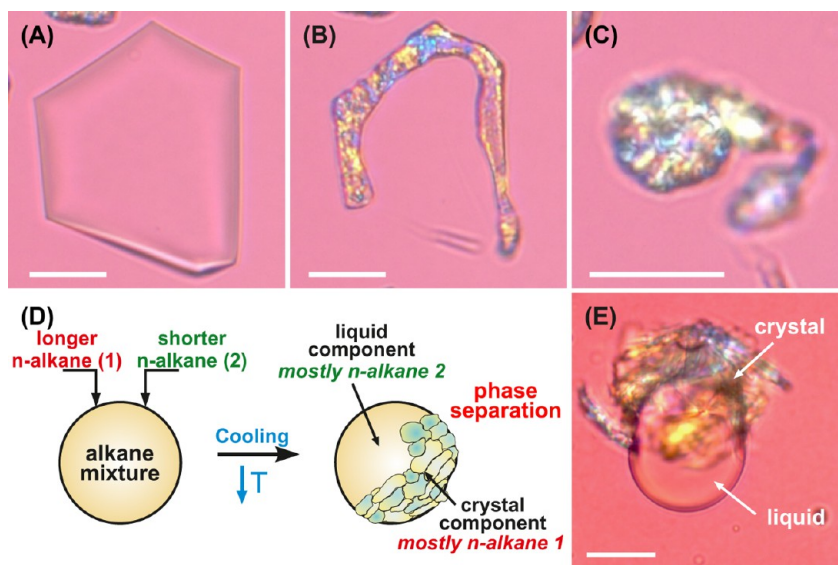


Figure 6. Freezing of multicomponent drops with $\Delta n > 4$. Fluid shapes are not preserved upon freezing. (A–C) $C_{14}:C_{20} = 1:2$ v/v, stabilized by $C_{18}EO_{20}$, cooling rate 0.4 K/min. (D) Schematic representation of the phase separation process. Upon cooling two distinct regions are observed within the drops: a liquid part consisting mostly of the molecules of the shorter alkane and a frozen crystal part from the longer alkane in the mixture (E) $C_{14}:C_{20} = 2:1$ v/v, stabilized by $C_{18}SorbEO_{20}$ surfactant, cooling rate 4 K/min. Scale bars: 20 μm .

These experimental observations are in a good agreement with the phase diagrams obtained by Mondieig et al.,²⁰ according to which only rotator phases should be present in the range of temperatures studied. Thus, we explain the transparent parts of the particles and their homogeneous structure as due to the different type of final phase transition observed with multicomponent alkane drops ($\Delta n < 4$), viz. $R_{CX} + L \rightarrow R_{CX}$, instead of $R_{CX} + L \rightarrow S$, which is the case for single-component drops. The bright colors observed at the periphery of the multicomponent particles are due to the better order of the rotator phase which has been formed earlier during the drop shape evolution, and the molecules there had more time to pack properly. The proposed explanation is also in a good agreement with the observed linear shrinkage upon the final phase transition, which is around 10% for the single-component particles, whereas it is around 2–3% only for these multicomponent particles.

Multicomponent drops of alkanes with chain-length difference, $\Delta n > 4$, show different behavior upon cooling. They pass through several stages of the evolutionary scheme, but freezing is observed at a certain temperature. After this process, the “frozen” particles do not preserve their shape but usually shrink back to one or several spherical drops, covered with small crystallites (see Figure 6A–C, Video S1, and subsection Self-Emulsification for Multicomponent Mixtures). This is caused by the phase separation of the alkanes within the particle. In fact, when we observe the appearance of bright colors, indicating ordering of the molecules within the particle (Figure 6B), this is due to the solidifying mostly of the longer-chain alkane in the mixture. Because of the big difference between the melting temperatures of the two alkanes in these mixtures, the longer one solidifies while the shorter one remains in a liquid state (see Figure 6C). After this initial freezing, however, the rotator structure stabilizing the nonspherical shape of the particle is broken, the capillary pressure of the liquid alkane is not counterbalanced by the plastic phase anymore, and the liquid fraction acquires the shape with the smallest interfacial area, i.e., of a sphere. The phase separation of alkanes with $\Delta n >$

4 within single droplet can be observed even better if higher cooling rates are used (see Figure 6E).

To preserve the shape of particles from mixtures with chain-length differences greater than 4 C atoms, we can add to the binary mixture a third alkane, with an intermediate chain length. Indeed, this strategy was successful, and particles from such ternary mixtures, where interchain length differences are less than 4 C atoms, do preserve their shapes upon freezing (see Figure 7A,B).

We also performed experiments with drops containing all alkanes with chain lengths between 14 and 20 carbon atoms (i.e., seven-component mixture) mixed in equal volume ratios. Interestingly, drops from this very complex mixture also self-shape, passing through the known stages of the evolutionary scheme (see Figure 7C,D). These particles look like the particles from binary mixtures for which $\Delta n < 4$. This experiment proves that the behavior of a multicomponent mixture is not determined by the difference between the shortest and longest components in the mixture, but rather by the greatest difference, Δn , between any two neighboring in chain-length components in the mixture. If it is smaller than or equal to 4, then the behavior of the mixture would be as the behavior of a binary mixture with $\Delta n \leq 4$; otherwise, a phase separation in the crystalline phases will be observed upon freezing, and the particles will not preserve their shape.

All these observations show that the self-shaping phenomenon is present not only for single pure substances but also for various binary, ternary, and even more complex alkane mixtures. Thus, providing water-soluble surfactants with long enough hydrophobic tail, the same behavior can be expected from very complex mixtures of alkanes found in the nature, for example, waxes.

Self-Shaping of Nonalkane Multicomponent Drops.

Here we present briefly our results for the self-shaping phenomena, observed with mixtures of compounds from different homologous series.

Non-alkane compounds can be divided into two separate groups: one for the compounds which can exhibit the self-

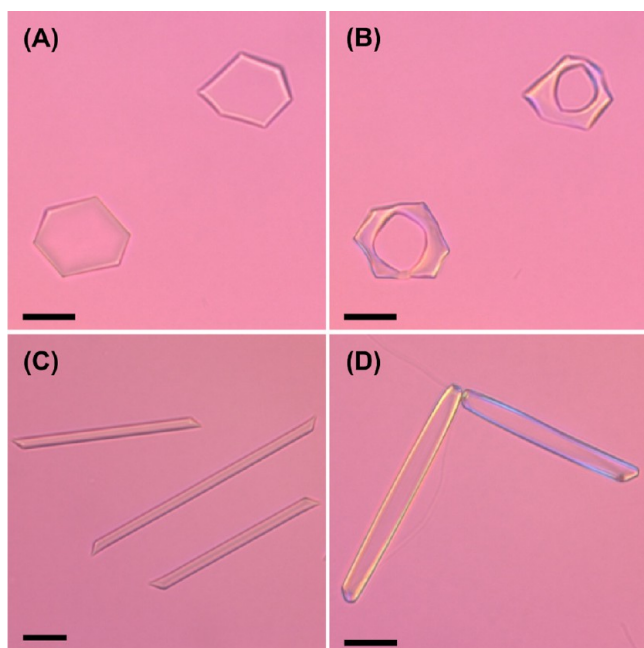


Figure 7. Preservation of the shape for multicomponent drops with $\Delta n > 4$. For mixtures with greatest chain length difference $\Delta n > 4$, the fluid shape can be preserved after the final phase transition, if a medium chain-length component is added to the mixture. (A–B) A ternary alkane mixture $C_{14}:C_{17}:C_{20} = 1:1:1$ v/v/v, stabilized by $C_{18}\text{SorbEO}_{20}$. (A) Fluid particles before their plastification. (B) Corresponding plastified particles. (C, D) A seven-component mixture from alkanes with chain lengths between 14 and 20 C atoms, mixed in equal volume ratios. (C) Fluid elongated tetragonal particles. (D) Plastified tetragonal particles. Scale bars: 20 μm .

shaping phenomena by themselves² in their pure state (group 1: triglycerides, alkyl-cyclohexanes, alkenes) and a second group

for the compounds which do not self-shape upon cooling (group 2).

Drops prepared from mixtures of compounds from group 1 self-shape upon cooling, passing through the known evolutionary scheme, no matter what is the volume ratio of the mixed oils (see Figure 8A–C). Particles prepared from them do preserve their shape upon their final phase transition (see Figure 8A–C).

To check the possibility for self-shaping of drops from mixtures of compounds selected from groups 1 and 2, we performed experiments with 1-tetradecanol mixed with hexadecane. For the stabilization of the prepared emulsions we used $C_{18}\text{EO}_{20}$ or $C_{18}\text{SorbEO}_{20}$ surfactants. Neither of these surfactants induces shape transformations in emulsion drops prepared with pure 1-tetradecanol. However, if 1-tetradecanol is mixed with hexadecane at a volume ratio of up to 85 vol % in favor of the 1-tetradecanol ($C_{14}\text{OH}:C_{16} = 85:15$), then shape transformations in the emulsion drops upon cooling are observed (see Figure 8D).

Furthermore, to check whether mixing a self-shaping compound with non-self-shaping compound always results in the possibility for self-shaping of the drops upon cooling, we performed additional experiments with substances that are found in nature, such as the complex mixtures of molecules found in cocoa butter, lard, and coconut oil. We observed drop shape transformations for all these substances if they are mixed with at least 15 vol % of alkane.

These results show the possibility for expansion of the self-shaping phenomena even beyond the many substances which self-shape in their pure state. They show that the self-shaping can be induced in many non-self-shaping substances if they are mixed with small amounts (e.g., with 15 vol %) of a self-shaping compound.

Melting. Melting of the multicomponent particles also has some specifics, as compared to the melting of those from single-

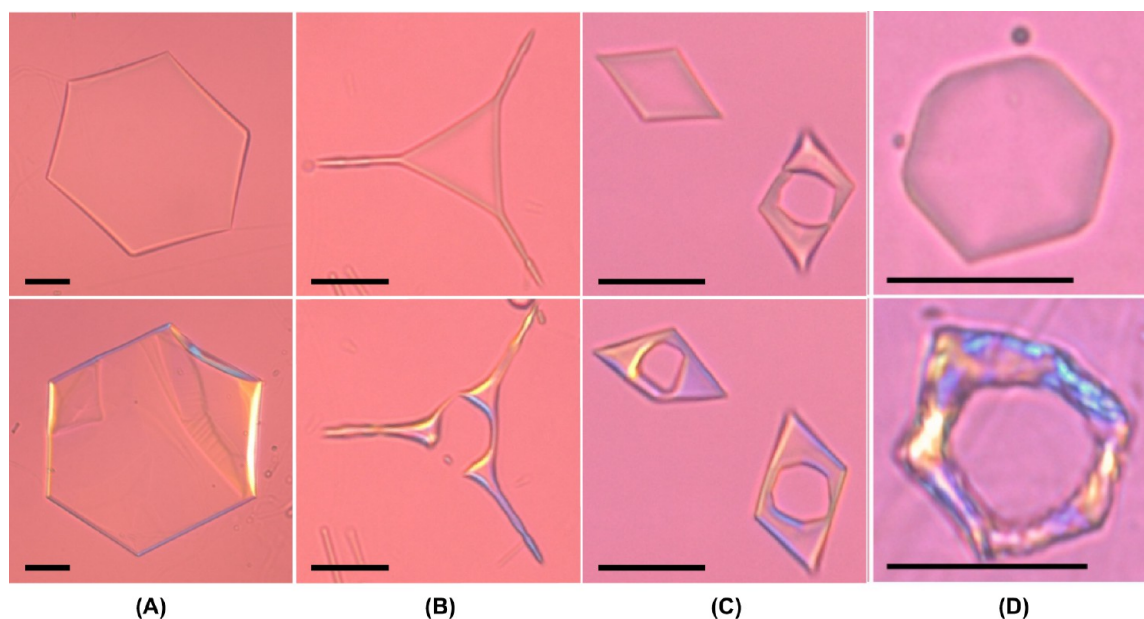


Figure 8. Self-shaping of various multicomponent drops. Upper row: fluid particles; lower row: frozen (plastified) particles. (A) Hexagonal platelet obtained from mixture of 1-eicosene and pentadecylcyclohexane in 2:1 volume ratio, surfactant $C_{18}\text{EO}_{20}$. (B) Triangular prism with protrusions obtained from mixture of pentadecylcyclohexane and 1-heptadecene in 1:3 volume ratio, surfactant $C_{16}\text{EO}_{20}$. (C) Tetragonal prisms (one of which has a hole in the center while still fluid) obtained from mixture of heptadecane and heptadecene, 1:1 volume ratio, surfactant $C_{18}\text{SorbEO}_{20}$. (D) Hexagonal platelet obtained from mixture of 1-tetradecanol and hexadecane in 85:15 volume ratio, surfactant $C_{18}\text{SorbEO}_{20}$. Scale bars: 20 μm .

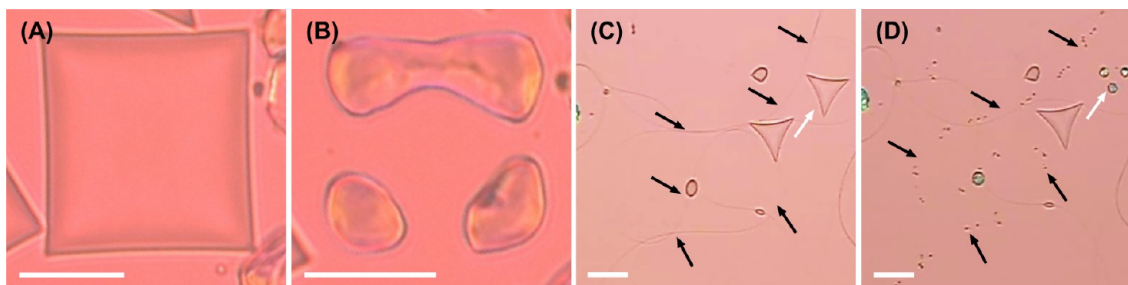


Figure 9. Disintegration of multicomponent drops with $\Delta n > 4$ upon freezing. Fluid shapes do not preserve their shape upon freezing. (A, B) $C_{14}:C_{19} = 1:1$ v/v, stabilized by $C_{18}\text{SorbEO}_{20}$. (C, D) $C_{14}:C_{20} = 2:1$ v/v, stabilized by $C_{18}\text{SorbEO}_{20}$. Scale bars: $20\ \mu\text{m}$.

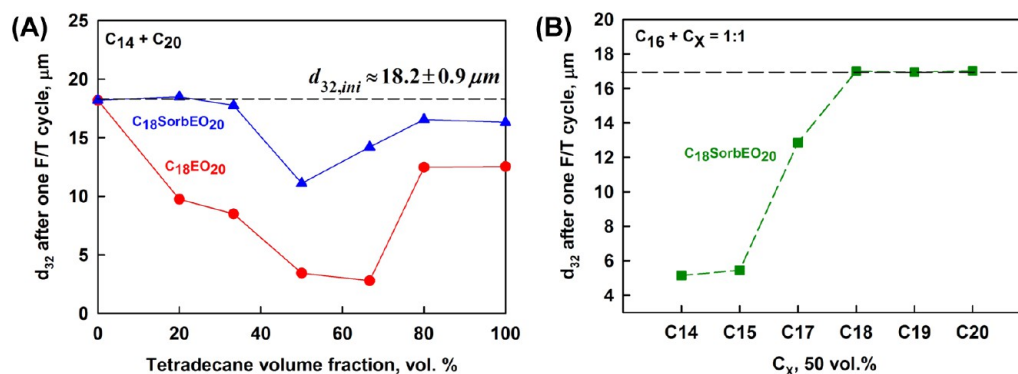


Figure 10. Drop size decrease in multicomponent mixtures. (A) Drop size decrease for the mixture $C_{14} + C_{20}$ in different volume fractions, cooling rate $\approx 0.45\ \text{K/min}$. (B) Drop size decrease for emulsion drops from 50 vol % C_{16} and 50 vol % other alkane. The emulsions are stabilized by the surfactant $C_{18}\text{SorbEO}_{20}$, cooling rate $\approx 0.45\ \text{K/min}$.

components. For single-component particles we always observe melting within a very narrow temperature range ($T_m \pm 0.2\ \text{K}$). In contrast, the multicomponent drops melt over a temperature range, the width of which depends on Δn . The wider chain-length distribution in the mixture, the wider the temperature range of melting is.

The temperature range of melting is always between the melting temperatures of the pure compounds. For mixtures with $\Delta n < 4$, usually it is within $4^\circ\text{--}6^\circ$, and the process starts close to the bulk melting temperature of the shorter alkane (see Figure S3). As observed with particles prepared from C_{16} and C_{17} mixture, the colors of the particles disappear near the bulk melting temperature of the shorter alkane, indicating formation of a more disordered phase inside the particles. However, the nonspherical shape is preserved, showing that the melting occurs inside out. The nonspherical shape disappears only when the bulk melting temperature of the longer alkane is reached, and the particle melts back into a spherical drop.

For mixtures with $\Delta n > 4$, when phase separation is observed, the temperature range of melting can be as wide as the difference between the bulk melting temperatures of the pure alkanes. For example, when mixing tetradecane and eicosane in equal volume ratio, the melting process is observed from 5 up to $37\ ^\circ\text{C}$. Because of the wide temperature range within which the melting process takes place, formation of some irregular nonspherical shapes without colors is observed upon heating. These irregular particles are stable over a wide temperature interval until the final melting into a spherical drop is observed.

Self-Emulsification for Multicomponent Mixtures. The self-shaping of mixture drops to nonspherical shapes can also lead to nonequilibrium phenomena, such as self-emulsification

via freeze–thaw cycles.³ By cooling and heating of the sample, we realized a self-emulsification process in which the drops significantly decreased their diameter. Three mechanisms were observed to be cooperative in the self-emulsification of single-component drops: repeated breakage upon cooling (mechanism 1), and fiber disintegration (mechanism 2) and melt–crystal fragmentation (mechanism 3) upon heating.³ All these three mechanisms are observed with multicomponent drops as well.

In addition, for mixtures of alkanes with chain-length difference greater than 4 carbon atoms, a fourth, very effective mechanism is observed: disintegration of the fluid shapes upon freezing (see Figure 9 and Video S1). This phenomenon has the same origin as the one described in section *Freezing of multicomponent drops with $\Delta n > 4$* . Because of the big temperature difference between the freezing temperatures of the oils, they phase separate upon freezing and mainly the long-chain component freezes while the short-chain alkane remains in a liquid state. In the moment of freezing of the long-chain component, the internal structure of the fluid nonspherical particles is destroyed, and several smaller drops and particles are formed as a result of capillary instability.

We performed systematic experiments to study this mechanism by varying the alkane ratio in the mixture of C_{14} and C_{20} , with the surfactants $C_{18}\text{SorbEO}_{20}$ and $C_{18}\text{EO}_{20}$. The respective results are presented in Figure 10A. The most effective self-emulsification is observed for volume fraction of the shorter alkane from around 50 up to 70 vol %.

In the emulsions stabilized by $C_{18}\text{SorbEO}_{20}$, for up to 40 vol % C_{14} , mechanism 3 (melt–crystal fragmentation) is the most operative one; it is facilitated by the presence in the drops of two alkanes with very different freezing/melting temperatures.

Upon freezing, mixed crystals are formed from the platelets (see Figures 3A and 6C) which consist of two different types of crystal domains: one which forms when mainly C_{20} freezes at high temperature and another one forming upon freezing of C_{14} at lower temperature. During the subsequent heating of the frozen particles, the C_{14} -enriched domains melt first, and small liquid drops are formed from them. The crystal structure of the frozen particles is destroyed as we raise the temperature, and separate C_{20} -enriched crystals are formed which eventually melt into multiple droplets.

When the C_{14} volume fraction is 50 vol %, many drops evolve up to the final stages of the evolutionary scheme upon cooling, but preservation of the shape is not possible when they freeze; the particles disintegrate and form many small crystals. At this volume ratio all four mechanisms are operative, resulting in the smallest drops after heating (see Video S1). With increasing the tetradecane volume fraction, later stages of the evolutionary process are observed, but in the final stages of the evolutionary scheme most of the oil is confined in a single ellipsoidal drop that extrudes thin fibers. Upon freezing these ellipsoidal drops form one frozen particle which upon subsequent heating melts into a single drop. These drops have almost the same diameter as the initial drops from which they have been formed. Therefore, in these systems the drop size decrease is mainly due to the fiber disintegration upon freezing (via mechanism 4) which is not too effective for decreasing the mean volume-surface diameter, d_{32} . At 100 vol % C_{14} , all drops easily evolve to the final stage of the evolutionary scheme, and no drop breakage upon cooling is observed; the drop size decrease in this system is due only to the fiber disintegration upon heating (mechanism 2).

The drop size decrease for C_{14} – C_{20} drops, stabilized by the surfactant $C_{18}EO_{20}$, is more pronounced due to the easier evolution of these drops (see Figure 3A). At 0 vol % C_{14} , the drops freeze in almost spherical shapes which melt back into drops with the same size as the initial ones; i.e., no drop size decrease is observed. For up to 35 vol % C_{14} , the drop size decrease is due to melt–crystal fragmentation which occurs over the wide temperature interval during melting. When C_{14} volume fraction is above 50 vol %, all drops easily reach the final stages of the evolutionary process. The observed difference between the drop size decrease for the samples with 50–70 vol % C_{14} (d_{32} after one cycle $\approx 4 \mu\text{m}$), and those with above 80 vol % C_{14} (d_{32} after one cycle $\approx 13 \mu\text{m}$) are due to the action of the newly found mechanism 4 as well as to the difference in the diameters of the fibers which are extruded from the ellipsoidal drop at the last stage of the evolutionary process. The particles in the samples with 50–70 vol % C_{14} cannot preserve their shape upon freezing, so many separate particles are formed upon the final phase transition. In addition, the extruded fibers in these samples are with diameter between 1 and $3.5 \mu\text{m}$, transferring a relatively large part of the oil into the fibers. In contrast, in the samples with greater volume percentage of C_{14} ≥ 80 vol %, we observe extrusion of fibers with smaller diameter ($d < 0.7 \mu\text{m}$) which do not disintegrate upon freezing. The main fraction of the oil remains in the ellipsoidal drops which freeze and then melt back into single drops. The drop size decrease is insignificant in these last systems.

As shown in Figure 10A, the most effective drop size decrease after one cycle is observed when the alkanes in the mixture are in equal amounts. To clarify the effect of the difference Δn in the mixture, we performed experiments with binary mixtures containing 50 vol % C_{16} and 50 vol % of

another alkane, with chain length varied between 14 and 20 C atoms. These experiments were performed with $C_{18}SorbEO_{20}$ because of the observed deep minimum in the drop size with this surfactant and the alkane mixture $C_{14}:C_{20} = 1:1$. As seen in Figure 10B, a significant drop size decrease is observed for the mixtures of hexadecane with tetradecane and pentadecane. This is due to the extensive drop shape evolution for these mixtures; the drops easily reach the final stages of the evolutionary scheme, so the self-emulsification mechanisms 2 and 3 are well pronounced. In the mixture $C_{16}:C_{17} = 1:1$ v/v, the drop size decrease is only due to the not very effective (in this system) mechanism 3. However, when the longer alkane in the mixture is with equal or longer chain length to that of the surfactant, the shape transformations of the drops are less pronounced and no drop size decrease is observed.

CONCLUSIONS

More than 80 different oil mixtures were used as the oily phase to study the self-shaping phenomena in multicomponent drops. The main conclusions could be summarized as follows:

Drop self-shaping is observed for all alkane mixtures (no matter whether they are binary or with more components) whenever the longest alkane in the mixture is with no more than 3 C atoms longer than the chain length of the surfactant hydrophobic tail. The shorter alkane could be of any length.

Self-shaping is observed also with mixtures of substances from different homologous series (e.g., alkane + alkene), if the pure compounds can self-shape upon cooling.

Transformations upon cooling can be induced also for substances which do not self-shape in their pure state, if they are mixed with substances which form drops that can self-shape upon cooling (e.g., 1-tetradecanol + alkane). The self-shaping process can be induced by adding only ca. 15 vol % of the self-shaping substance to the non-self-shaping one.

Multicomponent drops spontaneously transform their shape, passing through the same evolutionary scheme as single-component drops. However, with the mixtures, we also observe many regular platelets featuring 90° angles, which have not been commonly observed with the single-component drops.

Binary mixture alkane drops, prepared from alkanes with chain length difference $\Delta n \leq 4$, plastify upon cooling rather than freeze. This is due to the expanded range of stability of the rotator phases, formed in alkane mixtures, as known from the literature.^{15–17,19,20} These particles preserve their nonspherical shape upon plastification. When the oil mixture and surfactant tails pack very well at the interface, it is possible to observe initial plastification of the extruded protrusions only, transforming them from soft and flexible into straight and nonflexible fibers while the main body of the drops is still in a liquid state.

Upon freezing, drops from alkanes with $\Delta n > 4$ break into several separate spherical entities because of the phase separation (freezing of one of the components only) within these drops.

The behavior of drops with more than two alkanes is determined by the greatest difference gap, Δn , between the consecutive chain lengths in the mixture.

Melting is observed within a temperature interval, instead at a fixed temperature (as with single-component drops). Some nonspherical colorless shapes are observed under crossed polarizers, indicating that the particle surface contains mainly the longer chain-length components, while the shorter components are in the particle interior.

Upon thermal cycling, oil mixtures exhibit the self-emulsification process, reported recently for pure compounds.³ In addition to the three mechanisms already described—droplets breakage upon cooling, fiber disintegration, and melt-crystal fragmentation upon heating—a fourth new mechanism is observed with alkane mixtures. It is due to drop disintegration upon freezing for mixtures with gaps in consecutive chain lengths $\Delta n > 4$. This mechanism includes freezing of the different components at different temperatures, thus forming phase-separated crystalline domains of the longer and the shorter components. In the binary mixtures, the most efficient self-emulsification is observed when the surfactant stabilizing the emulsion is slightly longer than the longer alkane, and the alkanes are mixed in equal volume amounts because all four mechanisms are operative in these systems.

The whole study demonstrates that the self-shaping and self-emulsification are general phenomena and can be used not only for highly pure compounds but also for sophisticated mixtures and, if appropriate surfactants are chosen, even for waxes and compounds that do not self-shape in their pure state.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.7b01153.

Tables S1–S3 and Figures S1–S3 (PDF)
Video S1 (AVI)

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Notes

The authors declare no competing financial interest.

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