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Complex High-Internal Phase Emulsions that can Form Interfacial Films with Tunable Morphologies

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ABSTRACT: High-internal phase emulsions (HIPEs) were considered as an important functional material and have been the focus of intense development effort, but their fundamental attributes have hardly been altered at either the microcosmic or macroscopic level, which severely limits their practical applications in various areas. In this work, we report a general strategy for creating complex HIPEs that can form interfacial films at liquid interfaces. Double HIPEs and Janus HIPEs are both realized for the first time. They feature complex microscopic patterns with short-range anisotropy and exhibit non-Newtonian pseudoplastic flow behavior. By taking advantage of their response to a high-pH subphase, interfacial films can be successfully obtained, which are



tunable in thickness and morphologies under compression. Complex HIPEs can greatly expand the applications of liquid materials, and the interfacial films of droplets represent an important step toward producing 2D soft materials with a unique functionality that can be broadly applied to biological processes.

INTRODUCTION

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High-internal phase emulsions (HIPEs) are emulsified systems that have a large volume fraction of the dispersed phase and therefore feature microstructures spanning from close-packed spherical droplets to distinct polyhedral geometries. Compared to their dilute counterparts, these highly concentrated emulsions have a very large interfacial area, exhibit a unique viscoelastic behavior, and can be widely used as templates for key functional materials.¹ In the past decade, HIPEs have been the focus of intense research in both industry and biological sciences, in areas such as food products, cosmetics, organic semiconductors, and drug delivery systems.^{2–5}

Conventional HIPEs are a class of three-component soft matter, which contain one continuous phase, one dispersed phase, and necessary stabilizers to keep the system kinetically stable.⁶ In most cases, HIPEs are prepared by homogenous emulsification with immiscible water/oil pairs and are stabilized by low-molecular weight surfactants.' By learning from developments in other ternary systems, researchers working on HIPEs have made big steps forward in recent years. For instance, a broad range of colloidal particles, including silica particles,^{1,8,9} graphene oxide,¹⁰ microgels,^{6,11} assembled copolymers,¹² and protein-based particles,¹³ have been applied to stabilize HIPEs (i.e., pickering-HIPEs). The surface-active particles can adsorb irreversibly at the liquidliquid interface and thereby lower the total free energy, which greatly increases the systems' stability and expands their applicability. In addition to using different stabilizers, nonaqueous HIPEs have also been created successfully.' As an

important type of microreactor, they can be used to carry out water-sensitive or high-temperature reactions.⁷ Furthermore, besides homogenous emulsification, sonochemical synthesis has been demonstrated to be an alternative approach for fabricating HIPEs.¹⁴

These achievements, although they cover almost all aspects of HIPEs, have not altered their fundamental attributes, neither the microscopic pattern nor the macroscopic configuration. Correspondingly, the inherent limitations of conventional HIPEs also remain. For instance, because the droplets contain only one liquid domain, they do not have the capacity to hold chemically distinct materials.¹⁵ One area of progress is the formation of emulsified systems with multiple-component dispersed phases, whose internal microstructure can feature separated droplets (*i.e.*, different dispersed phases form mutually independent droplets),¹⁶ core–shell droplets with two or even greater hierarchies,^{17,18} or Janus droplets.^{16,17} Droplet geometry and composition have a crucial influence on the emulsion properties and functionality, making these complex emulsions increasingly important in various application fields.^{17,19} However, to the best of our knowledge,

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Figure 1. Confocal micrographs of the created double HIPE (a), the FITC-labeled continuous network (b), and the Nile red-labeled castor oil droplets (c). (d,e) 2D-FFT patterns of the continuous network (d, the green dashed lines and the arrow mark a ~6.8 μ m structure periodicity) and the random arrays of castor oil droplets in the same region (e). (f) Measured G' and G" of the double HIPE (blue), two silicone oil–HIPEs (50 and 1000 cSt, black), and one castor oil–HIPE (red). The inset illustrates the macroscopic configuration of the double HIPE. (g–i) Microstructures of the castor oil–HIPE, silicone oil–HIPE (50 cSt), and double HIPE, respectively. The scale bar is 50 μ m.

complex HIPEs with an anisotropic internal microstructure have not yet been achieved. On the other hand, the solid-like flow behavior caused by the close packing of droplets into distorted polygons makes HIPEs promising candidates for two dimensional (2D) soft materials, for example, a HIPE film,²⁰ but such implementations are also limited so far.

In this work, by including the second dispersed phase, we report for the first time complex HIPEs based on water (as the continuous phase), a pair of immiscible oils (as two dispersed phases), nanoparticles, and an anionic surfactant, sodium dodecyl sulfate (SDS). Double HIPEs and Janus HIPEs with anisotropic configurations can both be realized. We first present the unique viscoelastic properties of these multiphase systems and then discuss their formation mechanism. By dropcasting the formed complex HIPE on the surface of a high-pH subphase, interfacial films of droplets can be obtained. We demonstrate that the films can be one-droplet thick and exhibit a gas—liquid phase transition when being compressed in a Langmuir trough.

RESULTS AND DISCUSSION

Figure 1a demonstrates the microstructure of the created system when shearing 1.5 g of silicone oil, 1.5 g of castor oil, and 0.5 g of aqueous solution (water with 4 mg of SDS and 6 mg of silica nanoparticles) at 8000 rpm (\sim 13700 s⁻¹) for 40 s (see the Experimental Section). Spherical droplets of silicone oil (black) and castor oil (red) are closely packed as can be seen. The two different types of droplets, while fairly

comparable in size (average diameter of 6.5 \pm 0.8 μ m) and shape, appear to be mutually independent, that is, this is a double HIPE system. Similar to conventional HIPEs, the continuous phase (green) in this double HIPE forms a threedimensional (3D) network to stabilize the entire system; capillary water bridges bind and separate individual droplets as shown in Figure 1b. Although the distribution of droplets obtained from different oils is irregular in general, some random arrays of one type of droplets can still be observed within localized regions (Figure 1c). In such regions, where different types of droplets are not distinguished, analysis performed using two-dimensional fast Fourier transform (2D-FFT) patterns indicates a structure periodicity calculated to be ~6.8 μ m (as marked in Figure 1d),²¹ coinciding with the average diameter of the droplets. This periodicity disappears when only analyzing the castor oil droplets in the same region; the corresponding 2D-FFT pattern is illustrated in Figure 1e, where the spatial frequency has slightly higher intensity in both horizontal and vertical directions, reflecting a local orientation of the droplet arrays. This becomes more obvious when the arrays exhibit some ordering in the vertical or horizontal direction (Figure S1, Supporting Information).²² Together, these confirm a short-range anisotropy in the double HIPE's microstructure.

Figure 1f compares the linear viscoelasticity of two double HIPEs (blue), two "single" HIPEs formed just by silicone oil (black), and one HIPE of castor oil (red). All systems exhibit a general signature yield of stress materials;¹ the elastic modulus (G') and loss modulus (G'') are both linear for a large amplitude of strain. Clearly, the G' of silicone oil-HIPEs strongly depends on the oil's viscosity,^{19,23} and the G' of castor oil-HIPE is larger than both silicone oil-HIPEs. When using castor oil (viscosity ~ 600 cSt) and a less viscous silicone oil (50 cSt), the G' of the created double HIPE falls in between (blue circle). However, with a very viscous silicone oil (1000 cSt), the double HIPE exhibits a larger G' than both the "single" HIPEs (blue square). It indicates that the two internal phases have a synergistic relationship, making the combined system more than a simple summation of two "single" HIPEs. This is directly embodied in the radius d of the droplets. As shown in Figure 1g, d of the castor oil-HIPE is $2.7 \pm 0.2 \ \mu m$, while all HIPEs formed by different viscous silicone oils have a 3-4 times larger d (Figure 1h and Figure S2, Supporting Information). Mixing these two liquids remarkably decreases the size of the silicone oil droplets, making them comparable to the castor oil ones (Figure 1i and Figure S2, Supporting Information). Meanwhile, the synergistic effect evolves around the viscosity ratio between castor oil and silicone oil, which has been proven in previous studies of ternary polymer blends,^{24,25} although the related mechanisms are still not clear (see more discussions in Supporting Information).

For silicone oil of a particular viscosity, the viscoelastic properties of double HIPEs strongly depend on the mechanical energy employed during system fabrication. Its G' increases significantly with the shearing rate $\dot{\gamma}$ (Figure 2a); systems formed by vortex mixing ($\dot{\gamma} \sim 5100 \text{ s}^{-1}$) remain partially fluidic (Figure 2b). Figure 2c,d illustrates the microstructures of a fluidic system and a highly gelled system ($\dot{\gamma} \sim 12 \text{ k rpm or } \sim 20550 \text{ s}^{-1}$). For contrast, the images filtered out most of the fluorescent signal from Nile red and mainly show the network formed by the continuous phase. Clearly, in Figure 2c, the droplets are large ($d \sim 13.4 \pm 7.2 \mu \text{m}$), spherical, and have a large distance between each other (>4 μm). In other words,



Figure 2. (a) Measured G' of double HIPEs increases significantly with the shearing rate. (b) Sample formed by vortex mixing remains partially fluidic. (c,d) Microstructures of a fluidic system (c) and a highly gelled system (d). The fluorescent signal from Nile red is shown only inside the dashed box. (e,f) Janus HIPEs created by adjusting the interfacial tensions between the liquids. Some particles aggregate around the droplets (e, marked in yellow) when adding a modest amount of ethanol into the aqueous phase.

this system has a very low internal phase concentration (see the discussions in Supporting Information). By contrast, Figure 2d demonstrates a highly concentrated emulsion of small polyhedral droplets ($d \sim 2.9 \pm 0.8 \ \mu$ m), which can be recognized as a typical double HIPE.

Similar to most emulsion-based materials, interfacial tension σ plays an important role in determining the morphology of our systems. Adding a modest amount of ethanol to the aqueous phase can increase σ between water and the oils (Table S1, Supporting Information). As a result, the created HIPE exhibits Janus topology (Figure 2e). Ethanol can also modify the surface chemistry of the added nanoparticles, making them easier to adsorb at the oil–water interface. In this case, the interface can be more efficiently stabilized, and the created Janus droplets are hence smaller. Some aggregated particles (highlighted in Figure 2e) can be found around the droplets, making a heterogeneous network. This indicates that the system might be very close to an inversion point, which can also be explained by the changes in the interfacial tensions.

Janus morphology can also be achieved by using different oil pairs. Figure 2f demonstrates a Janus HIPE with sunflower oil (red) replacing the castor oil. Here, the Janus topology is associated with the decrease in σ between two oils (Table S2, Supporting Information).

Although playing an important role, interfacial tension alone cannot reveal the formation mechanisms for either double HIPEs or Janus HIPEs. As can be seen in Table S1 (Supporting Information), the measured interfacial tension between silicone oil and the aqueous phase is much higher than the other two values. In this case, according to the previous reports, these two phases should be separated because this costs less energy per unit area.^{16,26} Meanwhile, considering the very low volume fraction of water (~13.8%), the most energy-efficient strategy for our systems should be similar to the schematic illustration in Figure 3a. Nevertheless, such a structure has never appeared.

We believe that the formation of double HIPEs and Janus HIPEs is associated with three factors. First, the "real" interfacial tension. The high-speed shearing may induce the absorption of some surfactant-like molecules such as phospholipids from castor oil/sunflower oil at the oil-water interface, causing a significant lowering of its interfacial



Figure 3. Formation mechanisms for complex HIPEs and their response to the pH of a subphase. (a) Predicted strategy for our systems that cannot be realized. The solid and dashed lines represent, respectively, the oil–water interface and the oil–oil interface. (b,c) Phase behavior of a pipetted double HIPE at an air–water interface with different pH values upon initial spreading (b) and after two weeks (c). The red and blue rectangles mark a rapid and a slow complete phase separation, respectively.

tension. At present, this dynamically changing interfacial tension is challenging to measure, which makes the final morphology of our systems unpredictable. Second, the viscosity (ratio). A rule of thumb indicates that a liquid of the lowest viscosity always tends to be continuous;²⁷ phase inversion in a binary-component system occurs when the viscosity ratio between the components is close to 1.²⁸ Consistently, the aqueous phase in our systems always acts as the continuous phase (Figures 1a, 2c-f), instead of forming water-in-oil droplets as illustrated in Figure 3a. Third and most importantly, the stability of the liquid-liquid interfaces. It is not surprising that two miscible oils (e.g., silicone oil and isopropyl myristate) cannot be used to create complex HIPEs (see Figure S3a, Supporting Information). The stabilizers used in our systems, either SDS molecules or the silica particles, can only adsorb at the oil-water interface (marked with a yellow solid line, Figure 3a). The oil-oil interface, as marked with a yellow dashed line in Figure 3a, cannot be stabilized. In this case, oil-oil phase separation is certainly inevitable. On the other hand, complex HIPEs most likely are the equilibrium morphologies based on the influence and competition between these three factors. When replacing the silicone oil with mineral oil, which is a complex mixture of highly refined saturated hydrocarbons, the created HIPEs exhibit various micro-morphologies, including single-oil droplets, core-shell droplets, and Janus structures with different contact angles. Furthermore, the droplet size has a very uneven distribution (Figure S3b, Supporting Information). At room temperature, our complex HIPEs can remain stable for more than a year.

Here, we further discuss the roles played by SDS and the silica particles in our systems. As a widely used anionic lowmolecular weight surfactant (LMWS), SDS can adsorb at the oil-water interface rapidly, providing fast stabilization of emulsions via electrostatic repulsive forces.²⁹ This can be reflected in the data shown in Tables S1 and S2, where the interfacial tensions of various oil-water interfaces remarkably decrease in the presence of SDS. In fact, our complex HIPEs can be stabilized by SDS alone without any added colloidal particles (Figure S4, Supporting Information). However, after a few months, creaming is observed. To improve the stability, SDS and silica nanoparticles were both introduced into the aqueous phase. The used silica nanoparticles were synthesized in our laboratory. Because of their hydrophilic nature, they prefer to stay in the aqueous phase and form a viscoelastic 3D network (see the green phase in Figures 1a and 2c-f), which effectively delays drainage and protects the droplets against coalescence or coarsening.^{30,31} Figure S5 (Supporting Information) shows comparison of the measured G' for double HIPEs with and without nanoparticles. It is clear that the system with nanoparticles exhibits a higher G'.

Nowadays, the development of 2D soft materials is of scientific significance and industrial importance.^{32–34} Liquid interfaces, in this context, have become ideal platforms for different colloidal particles and amphiphilic molecules to accumulate/self-assemble into 2D films.³⁰ Nevertheless, thin layers of emulsion droplets are rarely achieved so far mainly because it is difficult to trap droplets at liquid interfaces. In recent years, the response of the system components to the pH of a subphase has been found to be an effective means of inducing interfacial trapping. Typical examples include the production of thin films of hydrophobic dipeptides and graphene oxide sheets.^{31,32} Because the complex HIPEs are stabilized by negative charges at the interface and a



Figure 4. Monolayer-like film of binary droplets (a) and the corresponding 3D confocal scan (b). Some droplet aggregations are marked in yellow circles. (c–e) Interfacial bilayer of oil droplets that can be focused on two different planes (c,d) (scale bar = 75 μ m) and its 3D scanning (e). (f) II–A isotherm of an empty interface (the red curve) and that of a film containing binary droplets (the black curve). (g–i) Interface at certain compression stages as marked in (f). (j,k) Gelled interfacial films with different thickness were compressed in a Langmuir trough.

nanoparticle-occupied viscoelastic network in the continuous phase, it should be possible to create an interfacial film of these droplets. To test this, an air-water interface with different pH values was prepared and a double HIPE was pipetted at it. Rapid phase separation occurs when the water pH is lowered with HCl (marked in the red rectangle, Figure 3b); slow but complete phase separation can also be observed on the pure water surface within 14 days (marked in the blue rectangle, Figure 3c). Intriguingly, the pipetted sample keeps its bulk shape on the surface of water when 1 M NaCl is added, neither spreading at the interface nor dispersing into the subphase (see the fourth sample, Figure 3b,c). The mechanism may involve the precipitation of SDS³⁵ or the interaction between Na⁺ and the particles.³⁶ A film of droplets is truly realized on the surface of a NaOH solution (~ 10 mM, pH ~ 10), where the droplets stay and spread uniformly (see the fifth sample).

Figure 4a (taken directly from the water surface) demonstrates that the trapped droplets retain their original size, shape, and the binary composition (red droplets are castor oil droplets and the rest are silicone oil droplets); no obvious break-up or coalescence was observed. Meanwhile, the network formed by the continuous phase disappears, making a very large area per droplet. However, the droplets do not distribute separately but connect with each other into arrays and random aggregations (marked in yellow). 3D scanning confirms that it is a monolayer-like film with most droplets being in the same plane (Figure 4b). By adjusting the amount of the spreading sample, or the available area of the interface, multilayers with more complex morphologies can be produced. Figure 4c,d illustrates the fluorescent castor oil droplets focused on two different planes, which suggests a bilayer structure (see also its 3D scanning, Figure 4e). Here, it seems that during the

interfacial trapping process, the silica particles can transfer to the surface of the droplets (green fluorescence in Figure 4c,d), consistent with the fact that complex HIPEs without silica particles cannot be trapped at any interfaces.

By compressing the interfacial sheets in a Langmuir trough, a surface pressure-area $(\Pi - A)$ isotherm is obtained (the black curve, Figure 4f). Similar to the phase behaviors of a particle monolayer, the interfacial droplets undergo a phase transition from a gas phase (where the available area to each droplet is large, Figure 4g) to a liquid phase (where the droplets become more closely packed and start to interact with each other, Figure 4h). Furthermore, compression leads to a more dense film at the interface (Figure 4i) and a significant increase in the measured Π . However, this increase cannot reach a high value, and the compressed film does not collapse like a jammed monolayer of hard-sphere colloids.³⁷ This can be related to the precipitation of SDS in a high pH environment, which makes the interaction between the droplets very weak. As a result, the droplets can easily re-arrange themselves and from a multilayer, similar to a 2D wet foam.^{38,39} Upon adding sodium alginate to the aqueous phase and using Ca²⁺ for ionic cross-linking, the created films exhibit more significant material properties. Thin films (~30 μ m) can be soft and smooth as silk (see Figure 4j); the thicker ones are highly elastic and form distinct wrinkles under compression (Figure 4k). Moreover, a thixotropy study of the double HIPEs reveals a hysteresis loop (Figure S6, Supporting Information), which indicates a partial structure recovery and is common in topical transdermal drug delivery systems.^{19,25,40} Therefore, using these films, we will be able to develop a new type of medical skin patch that can deliver from three different phases with mutually incompatible active ingredients.

With parallel but separate functionalities provided by multiple phases, the created complex HIPEs can greatly expand the applications of liquid materials in food, cosmetics, and medical engineering. The obtained interfacial films of droplets also represent an important step toward producing 2D soft materials with unique functionality. Such films will be able to transport/deliver components that are separately variably soluble in water, a vegetable oil, and a silicone oil. The heterogenous environments could be employed in composite fabrication—or in delivery applications where the chemical identity of the channels is maintained.

CONLUSIONS

The created double/Janus HIPEs are ideal combinations between conventional HIPEs and multiple emulsions. With parallel but separate functionalities provided by multiple phases, they have the capacity to hold chemically/functionally distinct materials, which greatly expands the applications of liquid materials in food, cosmetics, and medical engineering. Their spatial anisotropy can also utilize variations in surface chemistry and electric/magnetic susceptibility to produce anisotropic material properties on macroscopic scales, which are valuable for technologies such as electro/magnetophoretic displays. The obtained interfacial films of droplets also represent an important step toward producing 2D soft materials with unique functionality. Such films will be able to transport/deliver components that are separately variably soluble in water, a vegetable oil, and a silicone oil. The heterogenous environments could be employed in composite fabrication-or in delivery applications where the chemical identity of the channels is maintained.

EXPERIMENTAL SECTION

Materials. Silicone oil (10, 50, and 1000 cSt), fluorescein isothiocyanate (FITC)-dextran (average molecular weight 3000–5000, FD-4), and sodium dodecyl sulfate (SDS) were purchased from Sigma-Aldrich and used as received. Sunflower oil (chemical grade, batch number: BCBV5320) and castor oil were purchased from Sigma-Aldrich and dyed with Nile Red (Sigma). Deionized water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA).

Emulsification. 0.5 g of aqueous phase containing a low concentration of ~6 mg of silica nanoparticles (~150 nm in diameter, synthesized in the laboratory and fluorescently labelled with FITC) and ~4 mg of SDS was first prepared. Then, 1.5 g of silicone oil was added to the aqueous solution, followed by 1.5 g of castor oil. The entire blend was first stirred by vortex mixing (at ~5100 s⁻¹) for ~20 s and then sheared using an Ultra-Turrax homogenizer (IKA T18 basic) with a 10 mm diameter head operating at ~13700 s⁻¹ (8000 rpm) for 40 s.

Characterization. The imaging was performed using a confocal microscope (Leica, SP8, Germany) with a 10× objective (N.A. = 1.4). Fluorescence excitation was provided using a 488 nm laser (for FITC) and a 555 nm laser (for Nile Red); emission filters were used as appropriate. Interfacial tensions were measured using a pendent drop technique with an OCA-20 contact angle system (Dataphysics, Germany). Young's modulus of individual droplets was measured with a Piuma nanoindenter (Optics11, BV, the Netherlands). All pH values were measured using a FiveEasy Plus pH meter (Mettler-Toledo Instruments, Shanghai, China). The rheological experiments were performed on a TA Instruments AR 2000 rheometer (USA). A thixotropy study was carried out with an RST rheometer (Brookefield, USA). Surface pressure measurements were performed in a Langmuir trough (KSV) with symmetric barriers. The barriers were typically moved together at a rate of 5 mm/min.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.1c01355.

2D-FFTpatterns of the arrays of castor oil droplets, size distributions of different HIPE systems, thixotropic profile of the double HIPE, double HIPE stabilized by SDS alone, comparison of G' and G'' between systems with and without silica particles, measured interfacial tension values, and some discussions on the rheological properties of the HIPEs (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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