



THE UNIVERSITY *of* EDINBURGH

Edinburgh Research Explorer

Symbiosis between the components of a soft composite material responding to osmotic shock: the case of three-liquid systems

Citation for published version:

Chen, W, Clegg, PS & Li, T 2022, 'Symbiosis between the components of a soft composite material responding to osmotic shock: the case of three-liquid systems', *Journal of Colloid and Interface Science*, vol. 608, no. 2, pp. 1135-1140. <https://doi.org/10.1016/j.jcis.2021.10.086>

Digital Object Identifier (DOI):

[10.1016/j.jcis.2021.10.086](https://doi.org/10.1016/j.jcis.2021.10.086)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Peer reviewed version

Published In:

Journal of Colloid and Interface Science

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.



Symbiosis between the components of a soft composite material responding to osmotic shock: the case of three-liquid systems

Wei Chen,^{a,b} Paul Clegg^c and Tao Li^{*,a,b}

^a Wenzhou Institute, University of Chinese Academy of Sciences, Wenzhou, Zhejiang 325001, China.

^b Oujiang Laboratory (Zhejiang Lab for Regenerative Medicine, Vision and Brain Health), Wenzhou, Zhejiang 325001, China.

^c School of Physics and Astronomy, University of Edinburgh, James Clerk Maxwell Building, Peter Guthrie Tait Road, Edinburgh, EH9 3FD, UK.

Corresponding author.

E-mail address: litao@ucas.ac.cn

Abstract

Hypothesis

For conventional high internal phase emulsions (HIPEs) with an external osmotic pressure greater than Laplace pressure, once the osmotic balance is broken, the swelling or shrinking of the aqueous phase can easily trigger phase separation. Mixing two immiscible dispersed phases in a double HIPE can evolve differently following an osmotic shock, which is expected to create a synergistic effect that can frustrate the phase separation of the system.

Experiments

Osmotic responses of double HIPEs were studied at the surface of a NaCl solution at a range of molarities. Fluorescence confocal microscopy studies were carried out to track the responses on microscopic scales. Measurements on surface tensions revealed the interfacial behaviors of the used surfactant.

Findings

A synergistic effect is achieved by a symbiotic process between the dispersed oils, where one type of droplets become more stable and pack around the other ones to halt their coalescence. The essential drive comes from the adsorption/desorption of surfactant molecules at oil-water interfaces. By directly adjusting the osmotic pressure difference, transitions between osmotic down-shock and osmotic up-shock can also be realized. This symbiosis greatly expands the potential technological applications of multiple-liquid systems, and can be used to design novel multi-functional composite materials.

Keywords

Osmotic; HIPEs; Three-liquid systems; Liquid-liquid interface; SDS

1. Introduction

Combining multiple components together often creates a great variety of symbiotic phenomena. Besides the particle-surfactant combinations that have been widely used in emulsions, foams and non-equilibrium droplets [1-6], binary surfactant mixtures are also preferred to single surfactants because of their mutual roles in enhancing the solubilization of organic compounds and reducing interfacial tension (IFT) to ultralow values [7-9]. Combinations of two choline-based ionic liquids can more significantly improve the lubricity of an aqueous glycerol solution, demonstrating great antiwear and friction-reducing properties [10]. Very recently, by mixing two immiscible oils in an aqueous phase, we have realized a series of high internal phase emulsions (HIPEs) with complex morphologies [11]. Synergistic effects are generated between these two dispersed oils, making the complex HIPEs more than a simple summation of two “single” HIPEs. Fig. 1a-c illustrate a silicone oil-HIPE (droplet diameter $D_m = 22.1 \pm 0.7 \mu\text{m}$, the average distance between droplets $h \approx 3.1 \mu\text{m}$, Fig. 1a), a castor oil-HIPE ($D_m = 5.4 \pm 0.4 \mu\text{m}$, $h \approx 1.1 \mu\text{m}$, Fig. 1b) and a double HIPE system ($D_m = 6.4 \pm 0.8 \mu\text{m}$, $h \approx 1.2 \mu\text{m}$, Fig. 1c), respectively. In the previous work, we have demonstrated that, mixing two oils together can remarkably decrease the size of the silicone oil droplets, making them comparable to the castor oil ones. More intriguingly, when using a very viscous silicone oil (1000 cSt), the storage modulus (G') of the double HIPE is larger than both “single” HIPEs [11].

Fig. 1d and e illustrate a similar synergistic effect on the stability of these emulsions. Turbiscan Stability Index (TSI) is a statistical parameter calculated by summing variations in light transmission/backscattering in successive measurements as a function of sample height [12,13]. The lower TSI value, the more stable the system is. As can be seen, the TSI values increase for all samples, indicating the deterioration in their stability. Specifically, the castor oil-HIPE exhibits the lowest stability (the red curve in Fig. 1d), and the instability of the silicone oil-HIPE increases almost linearly with time (the black curve, Fig. 1d and e). For the double HIPE, however, its TSI values becomes lower than that of both “single” HIPEs after ~ 30 hours (the blue curve in Fig. 1e), suggesting a potential mechanism that exists in this combined system to effectively improve its bulk stability. The wavy and slightly erratic nature of the curves may be evidence for intermittent dynamics, not uncommon in dense soft matter samples.

In this work, we adopt an alternative strategy to explore the stability of a three-liquid system, which presents a symbiotic phenomenon that can be directly observed. It is widely recognized that the solid-like properties of HIPEs are due to the repulsive droplets have been compressed by an external osmotic pressure Π greater than the characteristic Laplace pressure ($2\sigma/R$, where σ is the IFT and R is the undeformed droplet radius) [14,15]. Meanwhile, for some complex emulsions (*e.g.*, water-in-oil-in-water emulsions), the gradient of osmotic pressure plays a major role in their stability [16]. Once the osmotic balance is broken, the swelling or shrinking of the aqueous phase (*i.e.*, osmotic down-shock or osmotic up-shock) occur, and the transfer of water molecules can easily trigger phase separation. However, in a concentrated system with three-liquids as illustrated in Fig. 1c, since various oils respond differently following an osmotic shock, the system would exhibit different phase behaviors compared to its “single” counterparts.

In fact, the changes in stability shown in Fig.1d and e can be seen as the behavior induced by the osmotic pressure gradient created by a gravitational field. More specifically, the continuous phase drains out of the system and collects at the bottom, making the droplets at the bottom small and essentially spherical, and large drops pack tightly at the top [17].

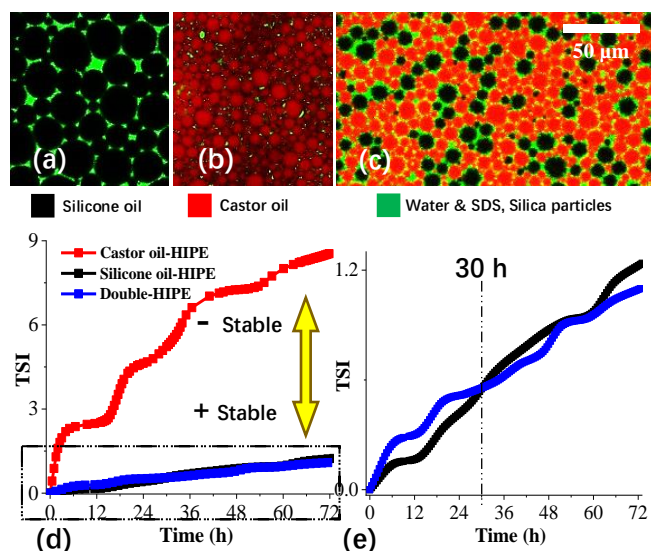


Fig.1. (a-c) The microstructure of a silicone oil-HIPE, a castor oil-HIPE, and a double HIPE, respectively. Reprinted with permission from [11]. Copyright © 2021 American Chemical Society. (d) Comparison of the TSI values recorded for various HIPEs at temperature of 25 °C. (e) A zoomed-in spectrum of (d, highlighted by the dashed square) for the silicone oil-HIPE (black) and the double HIPE (blue).

Herein, we demonstrate a mutually beneficial relationship created between various oils that can attenuate the osmotic shock response of a double HIPE. Specifically, the desorbed SDS from the castor oil-water interface can be utilized directly to enhance the stabilization of silicone oil droplets, making them super-stable even in a saltier environment. On the other hand, the super-stable silicone oil droplets can pack around the unstable castor oil droplets, forming a jammed protective layer to prevent their further coalescence and make the entire system stable. Microscopic observations reveal this symbiotic process, where the used stabilizers (i.e., silica nanoparticles and sodium dodecylsulfate, SDS) selectively adsorb or desorb from the liquid-liquid interfaces in response to the changes of IFTs. We also prove that the presented synergistic effect applies to osmotic down-shock, osmotic up-shock, and even back-and-forth between them. This work provides not only a realistic physical interpretation of the osmotic phenomena in double HIPEs, but also a strong evidence for the advantages of three-liquid systems. A broad range of liquid selection and their symbiosis can greatly expand the potential technological applications of soft materials.

2. Experimental Section

Materials. Silicone oil (50 cSt), Fluorescein isothiocyanate (FITC)-dextran (Mw = 3,000-5,000 g/mol, FD-4) and Sodium dodecylsulfate (SDS) were purchased from Sigma Aldrich and used as received. Castor oil was purchased from Sigma Aldrich and dyed with Nile Red (Sigma).

Deionized water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA). NaCl (99.99% metals basis) was purchased from Aladdin, China.

Emulsification. For a double HIPE system, 0.5g of aqueous phase containing ~6 mg of silica nanoparticles (~300 nm in diameter, synthesized in the laboratory and fluorescently labelled with FITC according to the methods described in Ref. [18, 19]) and ~4 mg of SDS was first prepared. Then 1.5g of silicone oil was added to the aqueous solution, followed by 1.5g of castor oil. The entire blend was first stirred by vortex mixing (at $\sim 5100\text{ s}^{-1}$) for ~20s, and then sheared using an Ultra-Turrax homogenizer (IKA T18 basic) with a 10 mm diameter head operating at $\sim 13700\text{ s}^{-1}$ (8000 rpm) for 40s. The “single” HIPEs were created by using ~3.0g silicone oil or castor oil, instead of both oils.

Characterization. The imaging was performed using a confocal microscope (Leica, SP8, Germany). All samples were transferred by a pipette and placed on a microscopy slide just before imaging. Fluorescence excitation was provided by 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 via a contact angle measurement system (Attension Theta Flex, Biolin Scientific, Sweden). A thixotropy study was carried out with an Anton Paar MCR 92 rheometer. The HIPEs' stability at temperature 25°C was evaluated using a Turbiscan Tower (Formulation, France), where the sample was put into a glass vial (1.2cm in diameter, 3.4cm in height) and the final TSI values were calculated by summing variations in the transmission and backscattering of light at the upper part (1/3) of the sample. The FITC fluorescence spectra were measured on a Fluoromax-4 spectrofluorometer (HORIBA Scientific) at temperature 25°C (excitation at 488nm and emission between 500 to 700 nm). For the droplet size and size distribution of each HIPE system, the diameter of more than 300 droplets were measured by hand using ImageJ software (<http://imagej.nih.gov/ij/>).

3. Results and discussions

3.1 Osmotic responses of a double HIPE system.

We first prepared a series of NaCl solutions with different molarities, and then drop-casted the created HIPEs onto their surfaces by using a pipette. Fig.2a illustrates the pipetted double HIPE at the interface. Because of the osmotic pressure difference between the NaCl subphase and the HIPE system (see a brief discussion on osmotic pressure in ESI†), osmotic response took place right after the drop-casting to achieve an osmotic balance. Here, three kinds of osmotic response were observed, which are osmotic down-shock (i.e., spreading), osmotic up-shock, and phase separation. Specifically, osmotic down-shock usually occurs at a low NaCl concentration; it leads to a net, rapid influx of water and the bursting of the HIPE system. In this case, the oil droplets spread directly at the interface and form a film (Fig.2b). Using a relatively high NaCl concentration results in osmotic up-shock, where the pipetted sample can keep its bulk shape, as shown in Fig.2c. When the NaCl concentration is even higher, very large oil domains can clearly be seen (Fig.2d), indicating a complete phase separation at the air-water interface. Strictly speaking, phase separation is not a direct response to the osmotic pressure difference.

We regard it as one for ease of comparison between the other two responses.

Table 1 illustrates the osmotic responses of various HIPE systems at a range of NaCl molarities. Consistent with the TSI measurements shown in Fig.1d, the castor-oil HIPE presents the lowest stability in the osmotic pressure gradient. Phase separation becomes unavoidable at all salt concentrations. The silicone oil-HIPE, however, exhibits all three kinds of osmotic response, which strongly depends on the molarity of the subphase. Compared to these “single” HIPEs, the osmotic response of a double HIPE has two notable features. First of all, at relatively low NaCl concentrations (*e.g.*, < 1.5M), no obvious phase separation was observed. That is to say, the instability of the castor oil phase causes no significant adverse effects. More intriguingly, at a higher salt concentration (~ 2.28M), where both “single” HIPEs undergo phase separation, the combined system “survived”. It exhibits osmotic up-shock and remains stable at the air-water interface (marked with a star in Table 1).

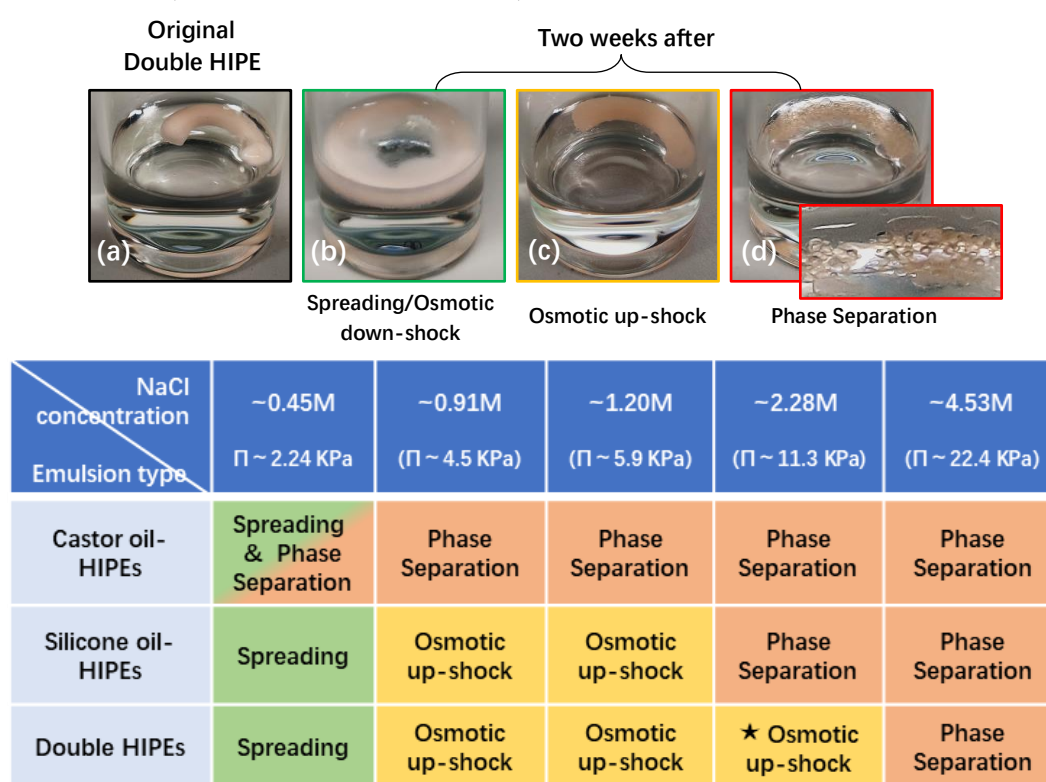


Fig.2. (a) The appearance of a pipetted double HIPE at the surface of a NaCl solution. The diameter of the glass vial is 2cm. (b) Osmotic down-shock leads to the direct spreading of the oil droplets at the interface. (c) Osmotic up-shock can keep the original bulk shape of the pipetted sample with a slight change in color. (d) A complete phase separation results in some visible large oil droplets. **Table 1.** The osmotic responses of various HIPE systems at different NaCl concentrations. Osmotic pressures of the NaCl solutions were calculated for each concentration (see a brief discussion in Supporting Information).

3.2 The Synergistic effect.

Fluorescence confocal microscopy studies were carried out to track the observed osmotic responses on microscopic scales. Fig.3a-d focused on the “single” HIPEs. The occurrence of osmotic down-shock dilutes the original silicone oil-HIPE, so that the osmotic pressure drops

well below the Laplace scale, leading to an emulsion of unpacked spherical droplets with large separation distances (h increases up to hundreds of micrometers, Fig.3a). On the contrary, osmotic up-shock can squeeze the continuous phase out of the system, where the droplets are deformed by the proximity of their neighbors, and therefore assume a polyhedral shape (Fig.3b). Particle aggregations can also be observed between the droplets (circled in yellow). Fig.3c and d illustrate the phase-separated states of the “single” HIPEs respectively, where no typical microstructures can be observed.

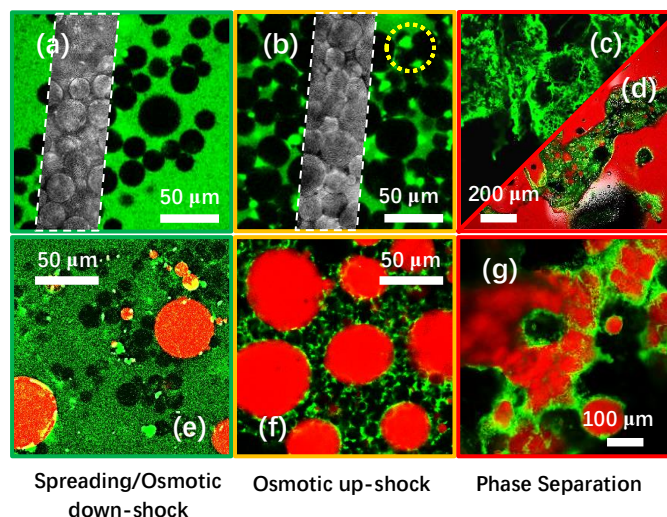


Fig.3. (a-c) Microstructures of a silicone oil-HIPE upon osmotic down-shock, osmotic up-shock, and phase separation, respectively. Observations by optical microscopy are shown in dashed squares. (d) The phase separated structure of a castor oil-HIPE. (e-g) Microstructures of a double HIPE upon osmotic down-shock, osmotic up-shock, and phase separation, respectively.

In the case of a double HIPE, osmotic down-shock also dilutes the system and leads to spherical droplets with large separation distances, as shown in Fig.3e. Again, particle aggregations can be found around the oil drops. Meanwhile, coalescence between the castor oil droplets can be easily noticed, which significantly increases their size from $\sim 6.4 \pm 0.8 \mu\text{m}$ (see Fig. 1c) to $\sim 23.5 \pm 17.5 \mu\text{m}$. Conversely, the size and size distribution of silicone oil droplets exhibit no significant changes. It has been observed that some of the silicone oil droplets can pack around the large castor oil droplets and thus help to prevent their further coalescence. This can be seen as a symbiotic phenomenon between the oils, which becomes more apparent and important for the case of osmotic up-shock. Fig.3f illustrates the microstructure of the double HIPE at NaCl concentration $\sim 2.28\text{M}$. As can be seen, all droplets pack together and deform, with a narrow layer of continuous phase separating them (see discussion below). Each large castor oil droplet is well “protected” by one or more layers of silicone oil droplets. Consequently, the entire system exhibits a better stability than both “single” HIPEs (marked with a star in Table 1). An even higher salt concentration ($\sim 4.53\text{M}$) promotes the coalescence of both dispersed oils and eventually leads to a complete phase separation (Fig.3g). See also Fig.S1, S2 and Table S1 (Supporting Information) for more related experimental observations on the synergistic effect (*e.g.*, a critical volume fraction of silicone oil).

3.3 Mechanisms.

To reveal the mechanism of the observed symbiotic process, we further tested the roles played by the used stabilizers. The created HIPEs were initially stabilized by both silica nanoparticles and SDS (see the Methods). The silica nanoparticles (~300nm in diameter) are labeled with FITC and generally prefer to stay in the aqueous phase because of their hydrophilic surfaces. Osmotic down-shock dilutes the continuous phase between the droplets, which accelerates the dispersing of the particles into the NaCl subphase. Fig.4a shows the fluorescence signal of FITC from the subphase at NaCl concentration ~0.45M. Strong signals were detected for all HIPE systems, where the fluorescence intensity for the double HIPE falls in between (the blue curve in Fig.4a). In the case of osmotic up-shock (NaCl concentration ~2.28M), however, the double HIPE exhibits the lowest fluorescence signal (Fig.4b), indicating that more particles stay in the emulsion instead of dispersing into the subphase. Due to partial screening, these particles adsorb onto the liquid-liquid interfaces and form a three-dimensional (3D) continuous network (see Fig.3f). This network, as a manifestation of the synergistic effect observed only in double HIPEs, can add yield strength to the background fluid and therefore enhances the stability of the system.

Compared with silica nanoparticles, SDS may play a more decisive role in the observed symbiotic phenomenon, since a double HIPE can be stabilized by SDS alone without adding particles [11], and such a double HIPE exhibits similar osmotic responses as the one with particles during the observation period (Table 1, see also Fig.S3, Supporting Information). As a widely used anionic low-molecular-weight surfactant, SDS can rapidly adsorb at the oil–water interface, with its apolar tail in oil, and the sulfate head group in water [20]. It remarkably reduces the IFT, and provides fast stabilization for emulsified systems *via* electrostatic repulsive forces [21]. It has been previously reported that, in the presence of NaCl, the critical micellar concentration (CMC) of SDS reduces remarkably. The free Na⁺ can bind to the sulfate head group of SDS at an oil-water interface (i.e., hindering dissociation). When the salt concentration is too large, SDS molecules can even be forced out of the interface due to “salting out” phenomena [22,23]. Since our experiments allow the diffusion of Na⁺ into the HIPE systems in both cases of osmotic down-shock and osmotic up-shock, the interfacial behaviors of SDS at different NaCl concentrations can be the primary mechanism of the observed synergistic effect.

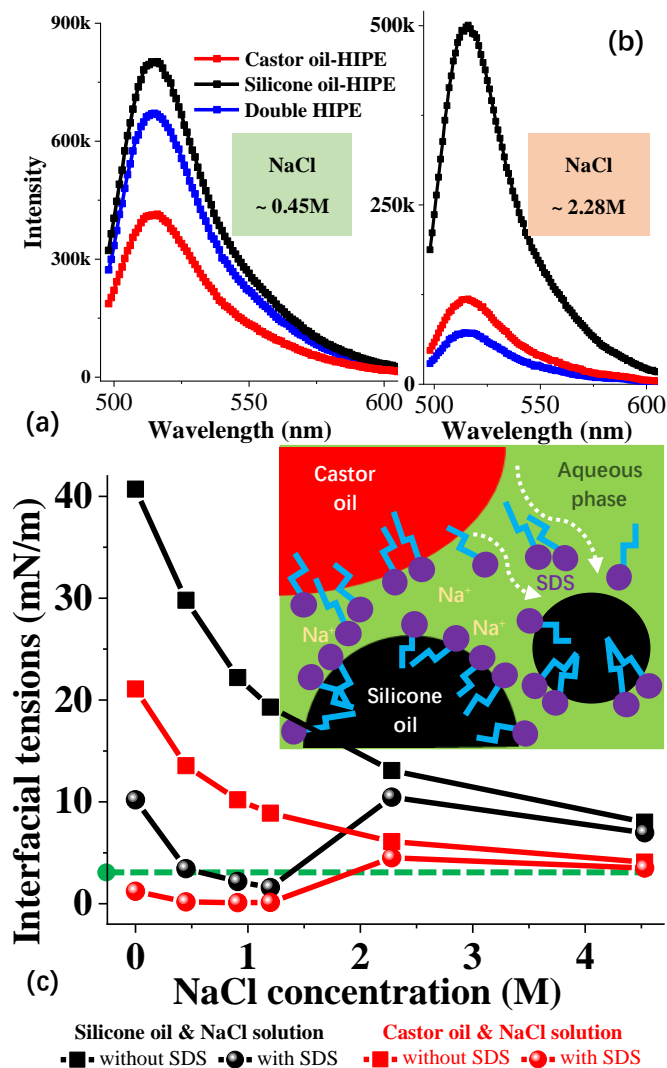


Fig.4. (a, b) The fluorescence single of FITC from the subphase at different NaCl concentrations. The measurements were carried out at the temperature 25 °C. (c) The IFTs between the oils and the aqueous phase change with NaCl concentrations. All data were measured without adding silica nanoparticles. The green line marks the IFT between silicone oil and castor oil (3.2 mN/m). Inset: SDS molecules desorb from the castor oil-water interface and re-adsorb onto the silicone oil-water interface (indicated by dashed lines and arrows).

Fig.4c illustrates the measured IFTs σ between the oils and a NaCl solution, which may reflect the interfacial behaviors of SDS in the absence of nanoparticles. When no SDS is added, the values of σ decrease with increasing the concentration of NaCl for both silicone oil-water and castor oil-water interfaces (solid squares). This might be due to the two main reasons following: firstly, inorganic salts can neutralize the surface charge at the oil-water interface in quantity, which obviously decreases the IFT [24]. Secondly, some impurities from the oil phase can be salted out at high NaCl concentration, which act as a surfactant and therefore decrease the IFT [25, 26]. For the silicone oil-water interface, adding SDS can continuously reduce the values of σ at low NaCl concentrations (≤ 1.2 M, black circles), confirming a relatively strong adsorption of SDS molecules at the interface. The binding between Na^+ and the sulfate head group of SDS can result in a closer packing of SDS, by reducing the repulsion between their charged head

groups [27]. Consequently, the created silicone oil droplets exhibit high stability at low NaCl concentrations ($\leq 1.2\text{M}$, see the osmotic responses for the silicone oil-HIPE in Table 1). For the castor oil-water interface, however, adding SDS barely change the values of σ in the concentration range from 0.45M to 1.20M (red circles, Fig.4c), indicating that the adsorbed SDS molecules are not stable and can easily desorb from the interface. This promotes the coalescence between the castor oil droplets, and causes the observed phase separation even at the lowest salt concentration (see the osmotic responses for the castor oil-HIPE in Table 1). At high salt concentrations ($>1.2\text{M}$), σ starts increasing for both oil-water interfaces; the increased values are very close to the systems without SDS, meaning that the surfactant molecules can barely adsorb onto the interfaces. Even the adsorbed ones can also be “salted out” by this concentration. As a result, the oil droplets are no longer stabilized and complete phase separation occurs inevitably.

The observed symbiotic process, *i.e.*, the responding of a double HIPE system to osmotic shock, can be a collaborative process mainly based on the interfacial behaviors of SDS at various oil-water interfaces. Although the diffusion of Na^+ can cause the desorption of SDS from the castor oil-water interface, the presence of silicone oil-water interface provides another choice for those desorbed molecules. As illustrated in the inset of Fig.4c (indicated by dashed lines and arrows), the desorbed SDS could be utilized directly to enhance the stabilization of silicone oil droplets. This also explains why the size and size distribution of silicone oil droplets exhibit no significant changes from either osmotic down-shock or osmotic up-shock. A tightly packed SDS film at the silicone oil-water interface, once formed, is difficult to destabilize by further increasing the salt concentration [27,28]. By squeezing the continuous phase out of the system, osmotic up-shock helps to pack the super-stable silicone oil droplets around the unstable castor oil droplets, forming a jammed protective layer as can be seen in Fig.3f. In the case of osmotic down-shock, the large separation distance can help to prevent coalescence between the castor oil droplets (Fig.3e).

3.4 Transitions between various osmotic shocks.

By directly changing the NaCl concentration in the subphase, transitions between various osmotic shocks can be realized in the same sample. Fig.5 demonstrates a transition from osmotic up-shock to osmotic down-shock. The double HIPE sample (1) was first pipetted onto the surface of a $\sim 1.20\text{M}$ NaCl solution and exhibited osmotic up-shock (Fig.5a and b). Two days later, water was added to the subphase to adjust its concentration to $\sim 0.91\text{M}$. This breaks the created osmotic balance in the system, and forces it to shift to a new balance. During the observation period (two days), a typical emulsion swelled significantly but still kept its bulk shape (Fig.5c). A small amount of oil phase was released at the interface (as circled in red, Fig.5c), which is likely to be caused by the rapid influx of water into the HIPE. Microscopically, the oil droplets were re-arranged with a larger separation (Fig.5d). Further decreasing the salt concentration to $\sim 0.45\text{M}$ leads to a standard osmotic down-shock (Fig.5e and f), where the HIPE was highly diluted and the oil droplets spread directly at the interface. Particle aggregations (*i.e.*, the bright green dots and domains in the confocal images) can be found

mainly around some large castor oil droplets.

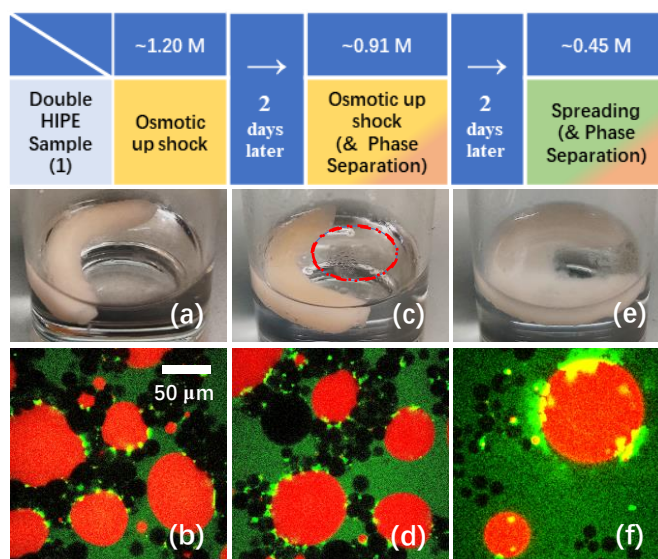


Fig.5. A transition from osmotic up-shock to osmotic down-shock by decreasing the concentration of the NaCl subphase (upper row). Appearance of the pipetted sample at the interface and the corresponding microstructures are illustrated in the middle row and the lower row, respectively.

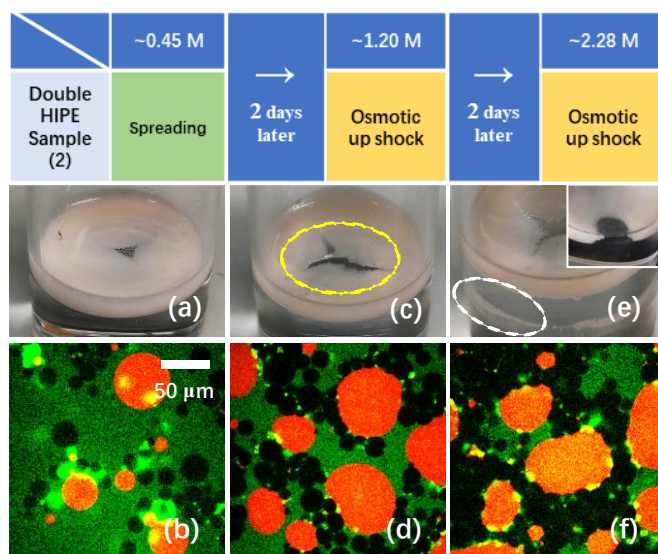


Fig.6. A transition from osmotic down-shock to osmotic up-shock by increasing the concentration of the NaCl subphase (upper row). Appearance of the pipetted sample at the interface and the corresponding microstructures are illustrated in the middle row and the lower row, respectively.

Fig.6 illustrates an opposite multi-step pathway. The double HIPE sample (2) initially exhibited osmotic down-shock at the surface of a ~0.45M NaCl subphase (Fig.6a and b), forming an interfacial film of oil droplets. Increasing the salt concentration into ~1.20M macroscopically grows the crack of the formed film (as circled in yellow, Fig.6c), and microscopically packs the oil droplets closer to each other (Fig.6d), indicating an osmotic up-shock of the spread system. These become more obvious when further increasing the NaCl concentration into ~2.28M

(Fig.6e and f). The interfacial film, after two rounds of osmotic up-shock, exhibits remarkable gel/solid properties. It can stick to the glass vial wall (circled in white, Fig.6e); Poking a hole on the film leaves an un-recovered fracture (see the inset of Fig.6e). Furthermore, since the oil droplets already spread at the interface, the diffusion of Na^+ into the film will be faster than that into a bulk sample. Therefore, the concentration of Na^+ around the interfacial droplets should be the same as that in the subphase (i.e., $\sim 2.28\text{M}$ in Fig.6f). In this case, the entire system still exhibits remarkable stability, confirming that the formed close-packing SDS film at an oil-water interface cannot be collapsed by simply increasing the salt concentration. By adjusting the amount of the spread materials, the interfacial area and the salt concentration, this strategy can be applied to produce interfacial gel films with tunable thickness and viscoelasticity.

4. Conclusions

Although it was known that combining various components together can sometimes create fascinating symbiotic phenomena [1,2,5-7], a symbiosis between the components of a soft composite material has not been reported. This work, building on the previous achievements on double HIPEs [11], presents such a symbiotic effect of various oils against osmotic shock, demonstrating an unusual route to prevent the phase separation of a three-liquid system. Compared to the “single” HIPEs [14-16], two dispersed phases can evolve differently following the osmotic balance, where one type of droplets pack around the other ones and therefore halt their coalescence. This collaborative phenomenon has been successfully captured by fluorescence confocal microscopy studies, and the physical mechanism which involves the interfacial behaviors of SDS molecules at different NaCl concentrations, is also revealed by measurements on surface tensions. By directly adjusting the osmotic pressure difference, a double HIPE can also exhibit a transition from osmotic down-shock to osmotic up-shock, and vice versa. This work highlights the advantages of multiple-liquid materials. With a broad range of liquids selection, symbiosis between various liquids can greatly expand the potential technological applications of soft matters, and can be used to design novel multi-functional composite materials. Further study will focus on more phase behaviors of three-liquid materials; phase-field simulations will be carried out for some fundamental mechanisms and more quantitative analysis.

Supporting Information

Supporting Information: A discussion on osmotic pressure calculation; more experimental observations on the synergistic effect; double HIPEs stabilized by SDS.

Acknowledgements

We thank Professor Ryohei Seto from Wenzhou Institute, University of Chinese Academy of

Sciences (UCAS) for useful discussions. This work was supported by the Young Scientists Fund of the National Natural Science Foundation of China (Grant No. 11904390) and the Scientific Research Starting Foundation from Wenzhou Institute, UCAS (WIUCASQD2020003).

References

- [1] B.P. Binks, J.A. Rodrigues, *Langmuir* 23 (2007) 7436–7439.
- [2] U.T. Gonzenbach, A.R. Studart, E. Tervoort, L.J. Gauckler, *Angew. Chem., Int. Ed.* 45 (2006) 3526–3530.
- [3] A.R. Studart, H.C. Shum, D.A. Weitz, *J. Phys. Chem. B* 113 (2009) 3914–3919.
- [4] T. Li, A.B. Schofield, K. Chen, J.H.J. Thijssen, J. Dobnikar, P. S. Clegg, *Chem. Commun.* 55 (2019) 5773–5776.
- [5] A. Toor, T. Feng, T.P. Russell, *Eur. Phys. J. E: Soft Matter Biol. Phys.* 39 (2016) 57.
- [6] J. Forth, P.S. Clegg, *Langmuir* 32 (2016) 6387–6397.
- [7] J.L. Cayias, R.S. Schechter, W.H. Wade, *J. Colloid Interface Sci.* 59 (1977) 31–38.
- [8] L. Zhu, S. Feng, *Chemosphere* 53 (2003) 459–467.
- [9] T. Qin, L. Goual, M. Piri, *Colloids Surf. A* 582 (2019) 123885.
- [10] D. Zheng, X. Wang, M. Zhang, C. Ju, *Tribology Letters* 67 (2019) 1–13.
- [11] T. Li, R. Xie, W. Chen, A.B. Schofield, P.S. Clegg, *Langmuir* 37 (2021) 9802–9808.
- [12] P. Bukrejewski, Z. Jarczewski, A. Matuszewska, *Archiwum Motoryzacji* 88 (2020) 5–18.
- [13] C. Sun, T. Wu, R. Liu, B. Liang, Z. Tian, E. Zhang, M. Zhang, *Food Hydrocolloids* 51 (2015) 512–518.
- [14] T.G. Mason, M.D. Lacasse, G.S. Grest, D. Levine, J. Bibette, D.A. Weitz, *Phys. Rev. E* 56 (1997) 3150.
- [15] C.P. Whitby, L. Lotte, C. Lang, *Soft Matter* 8 (2012) 7784–7789.
- [16] R. Mezzenga, B.M. Folmer, E. Hughes, *Langmuir* 20 (2004) 3574–3582.
- [17] H.M. Princen, *Langmuir* 2 (1986) 519–524.
- [18] N. Verhaegh, A. van Blaaderen, *Langmuir* 10 (1994) 1427–1438.
- [19] A. Imhof, M. Megens, J.J. Engelberts, D.T.N. de Lang, R. Sprik, W.L. Vos, *J. Phys. Chem. B* 103 (1999), 1408–1415.
- [20] H.B. de Aguiar, A.G.F. de Beer, M.L. Strader, S. Roke, *J. Am. Chem. Soc.* 132 (2010) 2122–2123.

- [21] S. Tesch, Ch. Gerhards, H. Schubert, *J. Food Eng.* 54 (2002) 167–174.
- [22] M.L. Corrin, W.D. Harkins, *J. Am. Chem. Soc.* 69 (1947), 683–688.
- [23] A.K. Chattopadhyay, L. Ghaïcha, S.G. Oh, D.O. Shah, *J. Phys. Chem.* 96 (1992) 6509–6513.
- [24] H.T. Zhou, Y.G. Zhu, T. Peng, Y.L. Song, J.B. An, X. Leng, Z.W. Yi, Y.Q. Sun, H. jia, *J. Mol. Liq.* 223 (2016) 516–520.
- [25] B. Gil, A.P. Handel, *J Am Oil Chem Soc* 72 (1995) 951–955.
- [26] A.G. Gaonkar, *J. Colloid and Interface Sci.* 149 (1992) 256–260.
- [27] Q. Xu, M. Nakajima, S. Ichikawa, N. Nakamura, P. Roy, H. Okadome, T. Shiina, *J. Colloid Interface Sci.* 332 (2009) 208–214.
- [28] S. Pandey, R.P. Bagwe, D.O. Shah, *J. Colloid Interface Sci.* 267 (2003) 160–166.