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Colloidal Particles at a Range of Fluid−Fluid Interfaces

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ABSTRACT: The study of solid particles residing at fluid−fluid interfaces has become an established area in surface and colloid science recently, experiencing a renaissance since around 2000. Particles at interfaces arise in many industrial products and processes such as antifoam formulations, crude oil emulsions, aerated foodstuffs, and flotation. Although they act in many ways like traditional surfactant molecules, they offer distinct advantages also, and the area is now multidisciplinary, involving research in the fundamental science and potential applications. In this Feature Article, the flavor of some of this interest is given on the basis of recent work from our own group and includes the behavior of particles at oil−water, air−water, oil−oil, air−oil, and water−water interfaces. The materials capable of being prepared by assembling various kinds of particles at fluid interfaces include particle-stabilized emulsions, particle-stabilized aqueous and oil foams, dry liquids, liquid marbles, and powdered emulsions.

■ INTRODUCTION

Colloidal particles of different types and shapes, ranging in size from a few nanometres to several micrometers, may assemble at the interface between two fluids, including cases where the fluids are both liquid and cases where one is liquid and the other is gaseous. Dispersed systems incorporating such particle assemblies include, inter alia, thermodynamically unstable particle-stabilized emulsions and particle-stabilized foams. These emulsifiers or foaming agents represent a very different class compared to more common examples such as low-molar-mass surfactant molecules and polymeric molecules. In particular, the latter typically adsorb and desorb from interfaces on a rapid time scale whereas solid particles, if large enough and of appropriate wettability, remain essentially irreversibly adsorbed in a quiescent system.[1] This has important consequences on the stability of drops and bubbles to coalescence and disproportionation, imparting kinetic stability such that demulsifying or defoaming these emulsions and foams requires new strategies. Particles may be surface-active but, unlike surfactant molecules, are not amphiphilic. The exception to this is the so-called Janus particles, i.e., heterogeneously coated particles possessing areas on their surface of different functionality, e.g., hydrophilic and hydrophobic, that are both surface-active and amphiphilic. Although reports on emulsions (so-called Pickering emulsions[2]) and foams[3] stabilized by particles appeared in the early 1900s, there was little activity in the area until around the 1970s, when a number of oil companies made the link between the ultrastability of crude oil−seawater emulsions and the presence (at least partially) of particles such as sand and clay at droplet interfaces present during oil extraction.[4] Of central importance is the wettability of the particles by both of the fluid phases, quantified by the contact angle the particle adopts at the interface, θ. For preferred emulsions containing equal volumes of oil and water, oil-in-water (o/w) emulsions form for more hydrophilic

particles in which $\theta < 90°$ whereas water-in-oil (w/o) emulsions arise for more hydrophobic particles in which $\theta > 90°$.

This Feature Article is not meant to be a review of the rapidly growing field of the behavior of particles at fluid interfaces but a brief snapshot of some of the more recent research from our laboratory, including external collaborations. For completeness, however, the reader is encouraged to look at recent reviews including those on stabilizing Pickering emulsions,[5] stimuli-responsive Pickering emulsions,[6] Pickering emulsions containing edible particles,[7] Pickering emulsion destabilization,[8] aqueous foams containing particles,[9] phase diagrams of liquid−fluid−particle mixtures,[10] liquid marbles (macroscopic liquid drops coated with particles),[11] contact angles of particles at interfaces,[12] and particles/particle−surfactant mixtures at fluid interfaces.[13] After working on surfactant-stabilized systems for some years, including microemulsions, emulsions, and foams, we began work on Pickering emulsions in 1998 within a Ph.D. project partially funded by an international paint company on pigment flushing between oil and water.[14] Our aim was to investigate mixtures of oil, water, and particles of high purity in order to establish the key principles behind the stabilization of emulsions and the arrangement of particles at both planar and curved oil−water interfaces. We progressed to mixtures of air, water, and particles and demonstrated the formation of novel materials such as dry water[15] along the way. The first research monograph on the behavior of particles at liquid interfaces was compiled in 2006 given the advances being made worldwide in a number of subareas.[16] The field has grown enormously this last 15 years or so, not only with an increase in the number of research groups becoming involved but in the
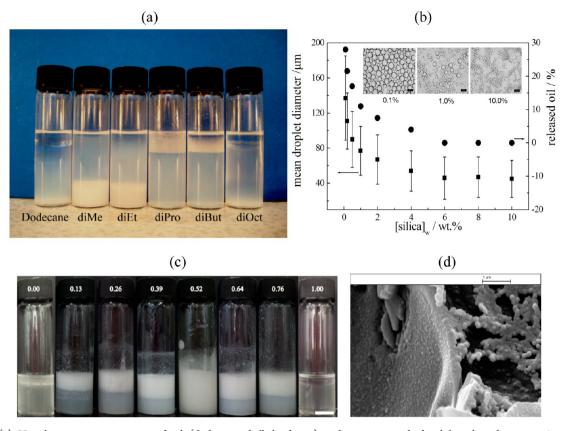
Table 1. Ways to Activate Charged Particles for Adsorption at Oil−Water Interfaces

strategy	particle type, primary diameter	oil	additive	main findings	ref
add salt in water	fumed silica (Aerosil 200), 12 nm	toluene	NaCl, LaCl$_3$, TEAB^a	1. salt addition improves emulsion stability to coalescence; (2) high emulsion stability when particles are weakly flocculated; extensive flocculation leads to destabilization	18
	pptd silica (Bindzil), 4−100 nm	heptane	CaCl$_2$	emulsion stability passes through the maximum with [salt]	19
	clay (Laponite RD), 30 nm	toluene, heptane...	NaCl	stable emulsions formed only when particles are flocculated	20
	polystyrene (carboxyl and amidine-coated), 1.9 and 0.4 μm	hexadecane	NaCl	1. carboxyl- w/o emulsion formed at ≥0.1 M; 2. amidine − stable o/w emulsion above 1 M	21
add salt to oil	Ag, Au, SiO$_2$, TiO$_2$, ca. 50 nm	DCM^b, hexane, toluene	TBANO$_3$,^{c} TBATPB^d	metal liquidlike films of particles form at planar interface	23
vary pH	fumed silica (Aerosil 200), 12 nm	toluene	NaCl (0−2 M)	maximum in emulsion stability at pH 4	18
	fumed silica (HDK), 20 nm	toluene		emulsions invert w/o → o/w on increasing pH	24
	polystyrene (carboxyl and amidine-coated), 1.9 and 0.4 μm	hexadecane	NaCl (10^{-3}−1 M)	1. carboxyl − no emulsion high pH; 2. amidine − no emulsion low pH	21
	polystyrene (di/triblock coated), 80−250 nm	dodecane, hexadecane		no emulsion at pH 2 but improving stability on raising pH	25, 26
	P4VP^e−silica microgel, 200 nm	dodecane, MM^f		stable emulsions at pH 8, no emulsion at pH 2 when microgels are swollen and charged	27−29
add alcohol to water	Au, 5−40 nm	heptane	ethanol	spontaneous assembly of particles by reduction of charge density	32
	Au, 13−100 nm	hexane	ethanol	highly ordered nanoparticle 2-D arrays form	33, 34
	Au, 16 nm	DCE^g	methanol	gold reflective film forms at interface	35
use of functional oil	fumed silica (HDK N20), 20 nm; pptd. silica (Ludox HS-30), 15 nm; zirconia, 5−10 nm	diallyl adipate (varied chain length)		1. dissolved oil molecules in water hydrogen bond with the particle surface, lowering their charge and increasing their hydrophobicity; 2. emulsion stability increases with oil solubility in water	36
add oppositely charged particles	pptd silica (Ludox HS-30), 15 nm	dodecane	pptd silica (Ludox CL), 15 nm	heteroaggregation of particles leads to flocs of low charge and increased hydrophobicity, which stabilize o/w emulsions	38
or	polystyrene (amidine), 0.5 or 2.2 μm	decane	polystyrene (carboxyl), 0.5, 3, or 9 μm	1. stable o/w emulsions formed at a particle number ratio of 1:1; 2. catastrophic phase inversion achieved at a number ratio of 1:1	39
mix oppositely charged polymers	PSSNa^h	dodecane, squalane, toluene	PDADMAC^i	1. spherical polyelectrolyte complex (PEC) particles (120 nm) form in water; 2. emulsions are o/w containing close-packed PEC particle layers	40
add oppositely charged surfactant	pptd silica (Ludox HS-30), 15 nm	dodecane	di-C$_{10}$DMAB^j	emulsions progress from o/w to w/o to o/w on increasing surfactant concentration	41
	Ludox HS-30, 15 nm	dodecane	CTAB^k	stable o/w emulsions at intermediate [surfactant] when particles flocculated	42
	Ludox CL, 15 nm	dodecane	SDS^l	maximum emulsion stability as flocculated particles coat oil drops in water	43
	calcium carbonate, 90 nm	toluene, octane	SDS	double emulsion phase inversion with increasing surfactant concentration	44
	pptd silica (Ludox HS-30), 15 nm	dodecane	di-C$_n$DMAB^m	multiple emulsions of w/o/w and o/w/o form near inversion boundaries for n = 12	45
	silica, 20 nm	toluene	various cationic surfactants	1. single chain or gemini surfactant: only o/w emulsion; 2. double chain surfactant: double emulsion inversion	46
	calcium carbonate, 90 nm	toluene	C$_n$COONa^n	increasing single emulsion phase inversion and eventually double phase inversion	47

Table 1. continued

strategy	particle type, primary diameter	oil	additive	main findings	ref
	silica, 20 nm	octane	DDA[o]	switching the surfactant between cationic and neutral forms with N_2/CO_2 is transferred to particles so that o/w emulsions are destabilized on demand	48
	silica, 400 nm	decane	di-C_{10}DMAB	contact angle of particles at interface passes through a maximum around conditions for emulsion double-phase inversion	49
	calcium carbonate, 90 nm	soybean oil	carboxylic acids	fatty acid impurities in commercial oil render particles hydrophobic, enabling o/w to w/o emulsion phase inversion	50
	silica, 20 nm	dodecane, toluene, tricaprylin	CTAB and SDS	particles hydrophobized by cationic surfactant stabilize o/w emulsion, which is demulsified on adding anionic surfactant	51
	silica, 20 nm	octane	AZO-B4[p]	1. stable/unstable o/w emulsion using N_2/CO_2 trigger; 2. UV or blue light increases or decreases drop size	52
increase inherent particle hydrophobicity	fumed silica (various HDK), 20 nm with increasing extent of silanization with short-chain silane	toluene		1. predictions based on detachment energy of a single particle relate directly to emulsion stability; 2. transitional phase inversion of emulsions (o/w → w/o) occurs on increasing the particle hydrophobicity; 3. most stable emulsions of smallest drop size formed around inversion; 4. catastrophic phase inversion of emulsions occurs on increasing the dispersed phase volume fraction	53
	fumed silica (various HDK), 20 nm	tricaprylin, Miglyol 812		1. no emulsion for extremes of wettability; 2. multiple emulsions with single particle type; 3. hysteresis of θ explains influence of initial particle location	54
	fumed silica (various HDK), 20 nm	various perfume oils		1. good agreement between calculated and exptl particle wettability for phase inversion; 2. transitional inversion from o/w to w/o induced by increasing particle concentration	55
	silica, 1 and 3 μm treated with silane reagent	octane		1. spread monolayers- particles aggregated at low θ, repulsive and well spaced at large θ; 2. Coulombic repulsion acts through oil phase	58

[a]TEAB is tetraethylammonium bromide. [b]DCM is dichloromethane. [c]TBANO$_3$ is tetrabutylammonium nitrate. [d]TBATPB is tetrabutylammonium tetraphenylborate. [e]P4VP is poly(4-vinylpyridine). [f]MM is methyl myristate. [g]DCE is dichloroethane. [h]PSSNa is poly(4-styrenesulfonate) sodium salt. [i]PDADMAC is poly(diallyldimethylammonium chloride). [j]di-C_{10}DMAB is didecyldimethylammonium bromide. [k]CTAB is cetyltrimethylammonium bromide. [l]SDS is sodium dodecyl sulfate. [m]di-C_nDMAB is dialkyldimethylammonium bromide for n = 8 and 12. [n]C_nCOONa is sodium alkyl carboxylate with n = 6−12. [o]DDA is N′-dodecyl-N,N-dimethylacetamidine. [p]AZO-B4 is 4-butyl-4-(4-N,N-dimethylbutoxyamine) azobenzene bicarbonate.
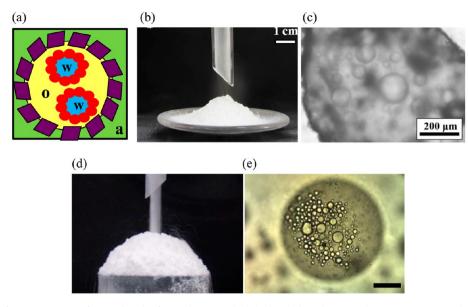
Figure 1. (a) Vessels containing mixtures of oil (dodecane, dialkyl adipate) and an aqueous hydrophilic silica dispersion 2 months after emulsification. (b) Variation of the average oil drop diameter (squares) and percentage of released oil (circles) with the silica particle concentration in water for o/w emulsions of diPro. The inset shows microscopy images, scale bar = 200 μm. Reproduced from ref 36 with permission from The Royal Society of Chemistry. (c) Appearance of emulsions after 2 weeks of dodecane in water, ϕ_o = 0.2, stabilized by PEC particles (20 g/L) of PSSNa and PDADMAC at different x_{PSSNa} values. (d) Cryo-SEM image of an emulsion in (a) at x_{PSSNa} = 0.52. Reproduced from ref 40 with permission from The Royal Society of Chemistry.

range of scientific disciplines too, including chemistry, food science, physics, chemical engineering, and material science. Taken from the Web of Science on February 23, 2017, the number of papers published in the period 1999−2017 with "Pickering emulsions" in their title was 651 along with 11 244 citations. In that period, the number of papers has increased exponentially, and citations exceeded 3100 in 2016. As a result, certain conferences have recently introduced a separate session/theme encompassing the field. The presence of particles at fluid interfaces in commercial products such as foodstuffs, pharmaceutical creams, and oilfield chemical formulations and in the industrially important process of froth flotation has been recognized for some time, but the precise role of the particles is unknown in many cases because of the complexity of the overall formulation that may contain surfactants, cosurfactants, polymers, or other solids. It is hoped that the fundamental understanding gained from the recent intense activity in the field will enable company researchers to both simplify existing products and design new formulations that take advantage of interfacially bound particles endowing the product with additional beneficial properties.

■ RECENT CONTRIBUTIONS

Our recent work and reference to that of others where possible is best summarized in terms of the different kinds of fluid−fluid interface-containing particles. They include the oil−water, air−water, oil−oil, air−oil, and water−water interfaces.

Oil−Water Interfaces. Because particles that are very well wetted by water and deemed highly hydrophilic do not in general adsorb spontaneously to oil−water interfaces or remain there even after temporarily engaging with it, one of our ongoing interests since the start has been to devise ways of activating such particles, rendering them surface-active. Many of the particle types are charged, e.g., silica, alumina, and polymer latex, and the magnitude of the charge is reduced in these modifications,[17] accompanied in most cases by particle aggregation in water. Whether these aggregates/flocs remain intact once oil is added and emulsions are formed depends on the amount of shear applied and on the specific components of the system, and it remains unanswered in many cases. Table 1 contains a summary of the eight different strategies developed to activate inherently hydrophilic particles such that they adsorb to the oil−water interface and become the stabilizer of emulsions. It includes details of the system and the main findings of the work. The addition of different salts to water is frequently employed, and o/w emulsions stable to coalescence can be produced under conditions where particles are weakly flocculated; extensive flocculation, however, leads to emulsion destabilization possibly because of the slow attachment of large flocs to freshly created interfaces during emulsification.[18−22] Recently, it was reported that various oils with dissolved oil-soluble salts containing organic ions when shaken vigorously with aqueous hydrophilic particle dispersions produced close-packed 2-D particle arrays at the planar oil−water interface.[23] The nanoparticles included anionic silica and metallic gold or
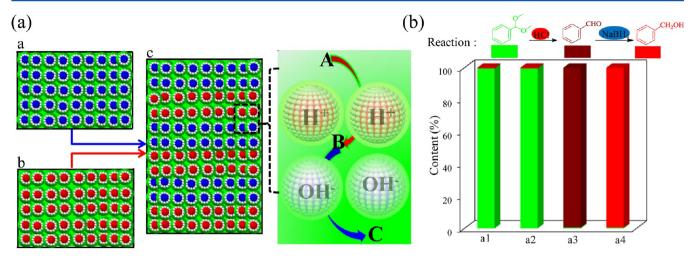
Figure 2. (a) Sketch of inner structure of a powdered w/o emulsion in which hydrophobic silica particles coat inner water drops and oleophobic clay particles coat outer oil globules dispersed in air. (b) Powdered water-in-squalane emulsion flowing through a glass funnel. (c) Globule of powdered water-in-olive oil emulsion showing inner water drops. Reprinted with permission from *Langmuir* **2016**, *32*, 3110. Copyright (2016) American Chemical Society. (d) Photograph of a powdered o/w emulsion in which dodecane drops are stabilized by partially hydrophobic silica particles and water globules are stabilized by very hydrophobic silica particles. (e) Microscope image of a water globule in air containing inner oil drops, scale bar = 200 μm. Reproduced with permission from Murakami et al. *Adv. Mater.* **2012**, *24*, 767. Copyright (2012) John Wiley and Sons.

silver in the presence of tetrabutylammonium cations or cationic particles such as titania and surface-modified metal particles in the presence of tetraphenylborate anions. These salts, called promoters, dissociate in oil, yielding ions near the interface of opposite charge to that of the particles. Any particles arriving from water to the interface partially submerge in the oil phase, and the Coulombic repulsion between interfacial particles is screened. This reduction in repulsion combined with the ever present van der Waals attraction allows the particles to pack closely at the interface and remain there. For particles containing ionizable surface groups such as −SiOH, −COOH, or −NH$_2$, changing the pH of the aqueous phase has also been used to effect particle activation.[18,21,24−31] At pH values around the isoelectric point (IEP) of the solid, particles are of low charge and are rendered more hydrophobic compared to pH values far from the IEP where they are charged and fully wettable by water. Particles of low charge stabilize o/w emulsions, and pH increases for silica particles can also trigger emulsion phase inversion from w/o to o/w.[24] Alternatively, short-chain alcohols such as methanol and ethanol when added to water (up to 50 vol %) result in the spontaneous assembly of charged metal particles to the oil−water interface to produce reflective films.[32−35] Alcohol molecules were deemed to reduce the charge density on particle surfaces by competitive adsorption in which charge stabilizing ions, e.g., citrate, are displaced from particle surfaces.

A new strategy was devised recently for enhancing the surface activity of hydrophilic oxide particles in water based on the use of a functional oil.[36] For dialkyl adipate oils used extensively in pharmaceutical formulations, it was shown that the limited solubility of the oil in water (higher for shorter chains) enables the functionalization of particle surfaces by physisorption with hydrogen bonds forming between the carbonyl group of the ester oil and the hydroxyl groups on particle surfaces. The dissolved oil molecules in water were shown to act like surfactant molecules (they lower the air−water tension) and reduce the zeta potential of the particles, leading to an increase in the oil−water contact angle. Figure 1a shows the appearance of o/w emulsions containing nanoparticles of silica, 15 nm, for different chain lengths of oil. No emulsion forms for dodecane (control) and dioctyl adipate (very low solubility), but emulsions of different coalescence stabilities form for dimethyl to dibutyl adipates. In the case of dipropyl adipate, Figure 1b shows the variation of the average drop diameter and the percentage of released oil with particle concentration. In line with other Pickering emulsion systems, the drop diameter decreases and reaches a limiting value by 6 wt % particles as the coalescence stability increases markedly. Heteroaggregation[37] of two kinds of hydrophilic particles of opposite charge was demonstrated to yield particle flocs of low charge and increased hydrophobicity compared to dispersions of either particle type alone.[38] Such flocs stabilized o/w emulsions in the case of nanoparticles (SiO$_2$ + Al$_2$O$_3$)[38] and microparticles (carboxyl-polystyrene + amidine-polystyrene).[39] We recently took this idea further by the in situ preparation of soft particles from oppositely charged water-soluble polymers, neither of which alone was capable of stabilizing an alkane−water emulsion.[40] For a mixture of two strong polyelectrolytes (PSSNa + PDADMAC), spherical polyelectrolyte complex (PEC) particles of diameter between 100 and 150 nm are formed in water through electrostatic interactions between the charged polymer chains. Around equal mole fractions (x) of the two polymers, the zeta potential reverses in sign and o/w emulsions for a range of oils can be prepared that are the most stable to creaming and coalescence. Figure 1c shows the appearance of emulsions after 2 weeks for different values of x_{PSSNa} ranging from 0 to 1. The cryo-SEM image in Figure 1d for x_{PSSNa} = 0.52 is recorded after sublimation of the frozen water, where it can be seen that PEC particles are densely packed at the droplet interface and excess particles form a network in the continuous aqueous phase.

Figure 3. (a) Schematic of a one-pot cascade reaction based on the layering of w/o Pickering emulsions. Red drops are those of a w/o emulsion with water-soluble acid and substrate A in the oil; blue drops are those of a w/o emulsion with a water-soluble base. By a layering procedure, cascade reactions can occur. A is the starting substrate, B is the intermediate, and C is the final product. (b) Final compositions of the deacetalization–reduction cascade reaction after 30 min at 25 °C. Green represents benzaldehyde dimethylacetal, brown represents benzaldehyde, and red represents benzyl alcohol. a1 represents the planar oil–water interface, and a2–a4 represent Pickering emulsions without HCl (2), without NaBH$_4$ (3), and with HCl and NaBH$_4$ (4). Reprinted with permission from *J. Am. Chem. Soc.* **2015**, *137*, 1362. Copyright (2015) American Chemical Society.

The adsorption of oppositely charged surfactant molecules to particle dispersions in water progressively hydrophobizes the particles, enhancing their surface activity at the oil–water interface.[41−52] For nanoparticles of anionic silica with a cationic surfactant[42,45,51] or cationic calcium carbonate with an anionic surfactant,[44,47,50] both stable o/w emulsions and in some cases w/o emulsions can be prepared. The phenomenon of double-emulsion phase inversion was reported as surfactant was added in increasing amounts,[41,44,46] and the direct measurement of θ showed that it passed through a maximum between the first and second inversion conditions.[49] More recently, stimuli-responsive surfactants bearing groups responding to N$_2$ or CO$_2$ bubbling[48,52] or UV light irradiation[52] were shown to transfer their responsiveness to particles after adsorption, eventually yielding stimuli-responsive emulsions that could be stabilized and destabilized on demand. The final strategy in this context is to employ particles of increasing hydrophobicity that are synthesized and characterized ex situ and then used as the stabilizer of emulsions[53−57] or to observe particle arrangement at the planar interface.[58] For silica or titania particles, this was achieved by chemisorption of the silane reagent to different extents, leading to particles exhibiting a progressive increase in θ. Both transitional phase inversion of emulsions (induced by changing the particle hydrophobicity)[53,57] and catastrophic phase inversion (brought about by changes in the oil/water ratio)[53] could be effected with such a series of particles.

By exploiting the irreversible adsorption of particles to different fluid interfaces, novel powdered emulsions that are lighter than their liquid counterparts can be prepared quite easily.[59,60] The process first involves the preparation of an emulsion stabilized by one type of particle that is then dispersed in air, a. The second step results in the breakup of the continuous phase of the emulsion into globules that require stabilization by a second type of particle. Thus, in the case of w/o emulsions (Figure 2a), high shear mixing produces a w/o emulsion stabilized by partially hydrophobic silica particles. If this is then shaken gently with oleophobic particles of fluorinated clay that are designed to adsorb to the air–oil surface, then a powdered w/o emulsion forms (w/o/a) that is free-flowing (Figure 2b) and whose oil globules contain interior

water droplets (Figure 2c).[60] In the case of o/w emulsions (o/w/a),[59] inner oil drops in water were stabilized by partially hydrophobic silica particles and outer water globules in air required very hydrophobic silica particles (Figure 2d,e). Because of the higher surface tension of water compared to that of oil, the second step required high shear homogenization to disperse water into globules. In both examples, the volume fraction and size of both droplets and globules could be controlled via particle concentration and the application of shear to the powder results in the release of water-rich and oil-rich domains. The method is favorable to traditional ones for surfactant-stabilized emulsions such as spray drying[61] because it does not require additional components or harsh processing conditions.

Chemical reactions involving catalysts taking place at a liquid–liquid interface are commonly carried out in mechanically stirred tank reactors. A major drawback is inhomogeneous mixing, and surfactants are often required to promote liquid–liquid contact. However, surfactants increase the environmental impact and carbon footprint of the process, and both product and catalyst recovery are usually difficult. Pickering emulsions of increased interfacial area and kinetic stability offer a green alternative, particularly if the stabilizing particles possess catalytic properties.[62,63] One goal in synthetic chemistry is to process multistep cascade reactions in a one-pot fashion as in living systems. A key challenge, however, is preventing the mutual destruction of opposing reagents, e.g., acid and base, so compartmentalization is crucial alongside allowing other reactants to diffuse freely. We put forward a novel strategy to achieve this based on a layered Pickering emulsion system.[64] As shown in Figure 3a, two w/o emulsions are prepared in which one contains dissolved acid in the drops and a reactant A in the oil whereas the other contains dissolved base in the drops. The layered architecture allows the positioning of droplets in different regions to avoid direct contact. During the reaction, reactant A diffuses through the oil phase and is converted to intermediate B on meeting acid at the droplet interfaces and is subsequently transformed to product C after meeting the base-containing drops in the neighboring layer. As an example, the deacetalization reduction of benzaldehyde dimethylacetal was
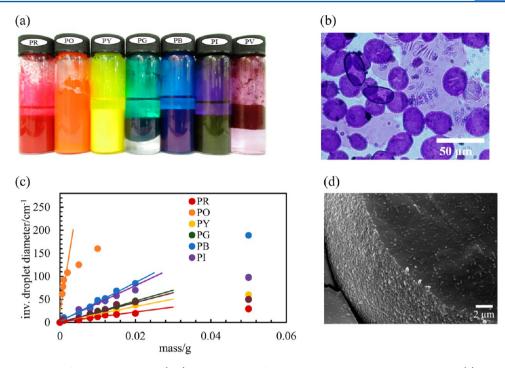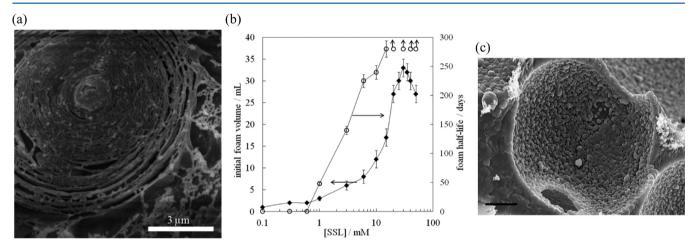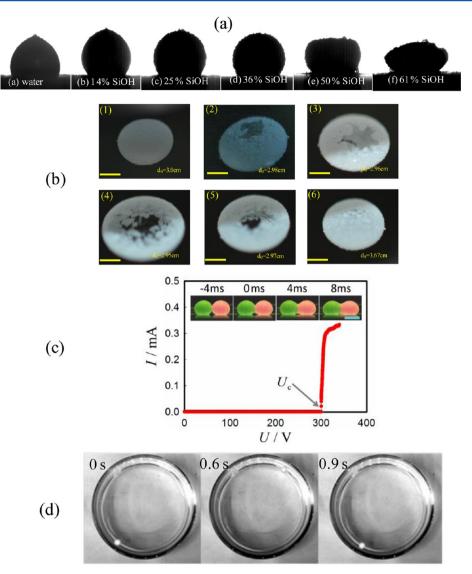
Figure 4. Pickering emulsions of heptane and water (1:1) stabilized by different organic pigment particles at 1 wt %. (a) Appearance 1 week after preparation in which emulsions are w/o except for PO, which is o/w; (b) Microscopy image of a w/o emulsion stabilized by PI; (c) inverse of mean drop diameter after 3 months versus the mass of particles for emulsions in (a), and (d) cryo-SEM image of a water drop in oil stabilized by PY. Reproduced from ref 67 with permission from The Royal Society of Chemistry.

Figure 5. (a) Cryo-SEM image of vesicles of the SSL surfactant in water at 30 mM, (b) initial aqueous foam volume (filled points) and foam half-life (open points) versus SSL concentration in mixtures with 1 wt % CaCO$_3$ particles, and (c) cryo-SEM image of aqueous foam stabilized by 30 mM SSL and 1 wt % particles. Reprinted with permission from *Langmuir* **2015**, *31*, 2967. Copyright (2015) American Chemical Society.

followed in which deacetalization to benzaldehyde is catalyzed by HCl and the reduction of this to benzyl alcohol is catalyzed by NaBH$_4$. After only 30 min at 25 °C, Figure 3b shows the content of the three compounds under different conditions. Virtually no product ensues if an emulsion is not formed (a1), whereas in the presence of both catalysts, 100% conversion to the product was achieved within a silica particle-stabilized Pickering emulsion (a4). Surface-active artificial enzyme particles were also designed and constructed as a new generation of interfacial biocatalysts for o/w Pickering emulsions, and their ability in biphasic biocatalysis was demonstrated.[65]

Pigments are particulate materials that have color-imparting ability and are largely insoluble in their medium of

application.[66] They are used extensively in products such as paint and cosmetics, but because these formulations contain other components, e.g., polymers and solvents, it is sometimes unclear if pigment particles remain in the bulk, reside at an interface, or partition between the two in the end product. The possibility of stabilizing emulsions of alkane and water with pure, colored organic pigment particles was explored recently.[67] Seven pigment types each possessing a primary color of the rainbow were selected. Their surface energies were estimated from contact angle data, and as expected, all were relatively hydrophobic except pigment orange (PO), which was relatively hydrophilic. Preferred emulsions at 1 wt % particles were w/o for the former and o/w for the latter (Figure 4a), in line with calculated contact angles being either side of 90°. Distinctly

Figure 6. (a) Shapes of a solidified bare water drop and liquid water marbles (15 μL) after cooling on a cold plate as the fumed silica particle hydrophobicity decreases. Reproduced from ref 74 with permission from The Royal Society of Chemistry. (b) Opening and closing of the PTFE particle shell on a liquid water marble (20 μL) under acoustic levitation. Photographs 1−3 show a cavity emerging on the surface and growing as the sound intensity increases, whereas photographs 4−6 show cavity healing and closing as the sound intensity decreases (scale bar = 1 mm). Reprinted with permission from *Langmuir* **2015**, *31*, 11502. Copyright (2015) American Chemical Society. (c) Evolution of the current passing through liquid water marbles (8.8 μL) coated with PTFE particles resting on glass upon increasing the voltage applied to them. Coalescence occurs on exceeding U_c = 300 V. The photographs show coalescence starting at 0 ms at U_c. Reproduced from ref 78 with permission from The Royal Society of Chemistry. (d) Motion of a 10 μL liquid marble (white) coated with fluorosilica particles containing 70 vol % aqueous ethanol placed on water. Reprinted with permission from *J. Phys. Chem. C* **2015**, *119*, 9910. Copyright (2015) American Chemical Society.

nonspherical water drops were observed with pigments indigo (PI) and violet (Figure 4b) as a result of the jamming of interfacial particles or the buckling of the particle layer preventing the relaxation of the droplet to a spherical shape.[68] The emulsion stability to coalescence increased with particle concentration, and they were shown to undergo limited coalescence from which the coverage of drop interfaces by particles was calculated (Figure 4c). The coverage varied from quite low to around a monolayer to possibly multilayers depending on the pigment. Consistent with this, a cryo-SEM image of a water drop in oil stabilized by pigment yellow (PY) reveals the presence of a close-packed particle monolayer. Importantly, pigment particles of size comparable to that in the powder adsorb to the interface, implying that high-shear homogenization is sufficient to disrupt aggregates in the

absence of a dispersant. We also showed that for pigments of intermediate hydrophobicity, catastrophic phase inversion is possible with emulsions inverting from w/o to o/w at higher water volume fractions.[67]

Air−Water Surfaces. The behavior of particles at air−water surfaces includes work on planar monolayers, aqueous foams, and liquid marbles. Although some of the principles learned with emulsions apply to foams, aerating a particle dispersion in water normally produces a low volume of foam compared to a typical surfactant solution. This is due in part to the fact that most particles do not lower the relatively high surface tension, so the breakup of air into bubbles is hindered. Because foams constitute many food products, there is growing interest in preparing particle-stabilized foams with new properties if food-grade particles can be sourced.[69] Calcium carbonate is edible,
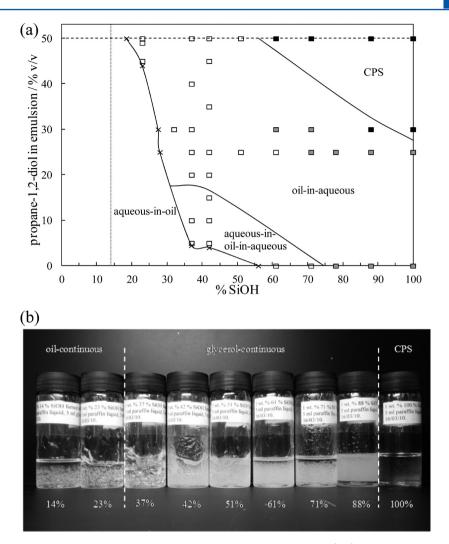
Figure 7. (a) Emulsion type and coalescence stability of paraffin liquid-propane-1,2-diol/water (1:1) emulsions stabilized by 1 wt % fumed silica particles of different hydrophobicities (given) for different contents of glycol. Dashed line, waterless emulsions; dotted line, most hydrophobic particles; CPS, complete phase separation. After 6 months, there is no coalescence (open points) or low coalescence (gray points). Reprinted with permission from *Langmuir* **2013**, *29*, 5723. Copyright (2013) American Chemical Society. (b) Appearance of emulsions of paraffin liquid and glycerol (1:1) stabilized by 1 wt % fumed silica particles after 1 month. The hydrophobicity of the particles is indicated by the relative silanol content. Taken from ref 83.

but its particles are too hydrophilic to adsorb at the air−water surface. In combination with low concentrations of an edible surfactant of opposite charge (sodium stearoyl lactylate, SSL), ultrastable aqueous foams result once particles become coated with a monolayer of surfactant.[70] SSL in water forms vesicles (Figure 5a), the bilayers of which contain surfactant chains in a solidlike state[71] such that the indestructible vesicles jam the aqueous films between bubbles, reducing drainage, coalescence, and disproportionation. The foamability of particle−surfactant mixtures increases with SSL concentration, reaching a maximum at 30 mM (Figure 5b). The highest foamability occurs when there is a significant population of discrete, nonaggregated coated particles as well as a high concentration of vesicles. Compared to foams of SSL alone (half-life ≤40 days), foam half-lives increase to over 280 days with very little foam decay or water drainage even after 1 year. In Figure 5c, a high coverage of surfactant-coated CaCO$_3$ particles (size 200 nm) at bubble surfaces that are mainly responsible for the high foam stability can be seen.

Inversion of the curvature of the air−water surface from a/w (foam) to w/a is possible if very hydrophobic particles are

chosen. The resulting bulk material is a powder termed dry water,[15] one macroscopic element of which is a liquid water marble.[72] Alongside the many applications of liquid marbles,[11] we have recently investigated different aspects including freezing,[73] levitation, coalescence, and self-propulsion. Liquid water marbles coated with fumed silica particles exhibit various shape transformations upon freezing depending on the hydrophobicity of the particles.[74] The shape can be recovered after remelting. For marbles stabilized by the most hydrophobic particles (low % SiOH), a vertically prolonged morphology with a pointed protrusion on top is formed and is similar to what is observed for a bare water drop (Figure 6a). For particles of intermediate hydrophobicity, the marble retains its original shape, whereas for relatively hydrophilic particles, flying saucer-shaped morphology develops.[73] We argued that the different responses to freezing arise from the different heterogeneous nucleation sites owing to the different positions of the particles at the air−water surface, i.e., θ. If the particles are more exposed to air (hydrophobic), then nucleation occurs on the convex surface of the particles that are very close to the cold plate. If the particles are more immersed in water (hydrophilic), then

ice embryos form in the concave cavities between particles. The volume expansion of water leads to lateral stretching of the particle network and ultimately to the horizontally inflated shape of the marble.
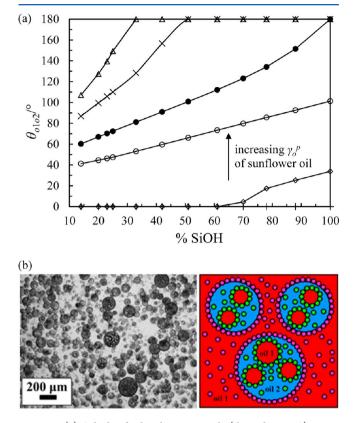
Because liquid water marbles are small reservoirs that can be transported without any leakage of the enwrapped liquid, they have great potential as microreactors.[75] In fact, they may be levitated in an acoustic field, enabling the opening and closing of their particle surfaces.[76] As seen in Figure 6b, upon increasing the sound intensity, particles migrate from the polar to the equatorial area of the droplet surface, leading to the formation of a cavity (1−3). Once a cavity forms, reagents may be added to the core of the liquid marble, and chemical reaction ensues. The cavity completely heals upon decreasing the sound intensity (4−6). The driving force for particle migration was shown to originate from the acoustic radiation pressure exerted on the portion of the particle surfaces protruding into air. Although manual manipulation of liquid marbles to move or coalesce has been demonstrated,[77] it is inefficient and tedious when a large quantity of sample is involved. On-demand and fast coalescence of liquid marbles controlled by external forces is highly desired. This was achieved by the use of a dc electric field.[78] Two contacting liquid water marbles can be forced to coalesce when charged by a sufficiently high voltage (Figure 6c). The threshold voltage depends on the size of the stabilizing particles (silicone) and the surface tension of the aqueous phase (varied with surfactant). By evaluating the electric stress and the surface tension effect, coalescence is attributed to the formation of a connecting liquid bridge due to the deformation of the surface at defects that subsequently grow, leading to the merging of the marbles. In addition, multiple marbles in a chain can be driven to coalesce, with the voltage required increasing linearly with the number of marbles; the air gap between adjacent marbles is treated as a capacitor.[78]

The autonomous locomotion of droplets driven by various physicochemical mechanisms has attracted widespread attention in the past decade. Among various mechanisms suggested, one involves the Leidenfrost effect, which takes place when a droplet is separated from a support by a vapor layer.[79] The self-propulsion of liquid water marbles containing high concentrations of ethanol and coated with oleophobic fluorosilica particles was evidenced recently.[80] When placed on a clean water surface, the marble moved rapidly rectilinearly (around 0.1 m s^{-1}), periodically bouncing elastically from the vessel side as seen in Figure 6d. After ca. 10 s, it rotated along the side of the vessel for 1 min and then stopped. The phenomenon is linked to the evaporation of alcohol from the marble because the velocity of motion increases with alcohol concentration in the marble, decreases with alcohol concentration in the subphase, and is independent of the volume of the liquid marble. The effect was explained by considering that the moving marble is isolated from the supporting water by a vapor layer. The evaporation of alcohol from the marble in the direction of $-x$ drives it in the direction of $+x$. In addition, alcohol that condenses on the free water surface lowers its surface tension, resulting in the Marangoni flow of subphase water in the direction of $-x$. This in turn enhances the evaporation, withdrawing vapor from the layer separating the marble from the liquid surface. This latter instability displaces the marble in the direction $+x$. The marble is stopped mainly by the viscous drag of the underlying water.[80]

Oil−Oil Interfaces. Emulsions that do not contain water are sometimes used as metalworking fluids that must exclude water and as chemical reaction vehicles involving reactants sensitive to the presence of traces of water. In the literature, water-free emulsions have been termed nonaqueous emulsions in which water (dielectric constant $\varepsilon = 78.5$ at 25 °C) has been replaced by a polar solvent such as glycerol ($\varepsilon = 42.5$), dimethylformamide ($\varepsilon = 36.7$), or ethylene glycol ($\varepsilon = 37.0$). Particle-stabilized emulsions can be prepared in such cases using hydrophobic silica or clay as a stabilizer.[81] However, certain pharmaceutical emulsions administered as creams to the skin contain high concentrations of polar glycol species such as propane-1,2-diol ($\varepsilon = 28.5$), where it is believed that such diols improve the solubility of the active ingredient and facilitate their transport across the skin surface. It is of interest, therefore, to ask about the progression of behavior in gradually replacing water by a polar solvent. In a systematic study of this kind, emulsions of paraffin liquid and aqueous propane-1,2-diol were stabilized by silica particles of different hydrophobicities.[82] For pure water systems, emulsions invert from w/o to o/w via multiple w/o/w emulsions upon decreasing the particle hydrophobicity to around 55% SiOH (Figure 7a, ordinate = 0). In pure glycol systems, however, transitional phase inversion occurs between 14 and 23% SiOH; otherwise, hydrophobic particles are rendered more hydrophilic (Figure 7a, ordinate = 50). Very stable oil-in-propane-1,2-diol emulsions, notoriously difficult to achieve with surfactants, were formed with particles of intermediate hydrophobicity, and the emulsion phase inversion may also be effected upon increasing the glycol content in the aqueous phase. Using calculated contact angles of particles at the oil−polar phase interface, reasonable agreement was found between measured and calculated phase inversion conditions assuming no glycol adsorption on particle surfaces.[82] Interestingly, replacing the diol by glycerol enables the preparation of stable and virtually transparent water-free emulsions of both types[83] because the refractive indices of paraffin oil (1.474) and glycerol (1.472) are very close (Figure 7b). Similar emulsions of low turbidity have been reported in ethylene glycol-tetradecane-copolymer worm particle systems.[84]

There are very few reports on mixtures of immiscible oils forming oil-in-oil emulsions where both oils have low dielectric constants, say ≤3.2, despite their use in cosmetics and personal care products.[85] One oil is usually a silicone oil (low intermolecular forces) in combination with either a paraffin or a vegetable oil. Some of the examples contain hydrophobic particles as the sole emulsifier,[86,87] but a detailed understanding of these systems is lacking. Because the oil−oil interfacial tension of between 1 and 3 mN/m is much lower than that of an alkane−water interface of >50 mN/m, the energy of detachment of particles from this interface will be reduced, posing a challenge for preparing stable emulsions. Despite this, fumed silica particles coated with either hydrocarbon or fluorocarbon groups were shown to be excellent stabilizers of silicone oil (S)−vegetable oil (V) emulsions.[85] Transitional phase inversion of emulsions, containing equal volumes of the two oils, from S/V to V/S occurs upon increasing the hydrophobicity of the particles. Close to the inversion condition, emulsions of minimum drop size are stable to coalescence and gravity-induced separation for over a year. Because it is difficult to measure θ for small particles at an interface, the contact angle θ_{o1o2} at the oil−oil interface (through S, o_2) was calculated using Young's equation and separating the surface energy terms for the solid and the oils into a polar and a dispersion contribution. It is anticipated that

in a system without water, the magnitude of any polar component will be crucial. Values of θ_{o1o2} are shown in Figure 8a as a function of the particle hydrophobicity (varied by % SiOH).
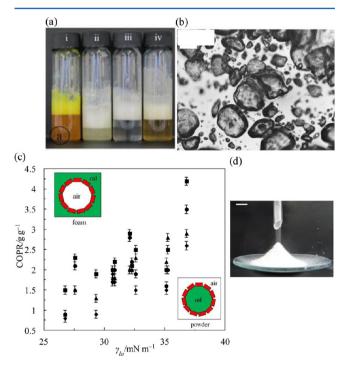

Figure 8. (a) Calculated oil−oil contact angle (through PDMS) versus % SiOH on silica particles for the interface sunflower oil−20 cS PDMS with γ_o^p; $\gamma_o^d = 0$; 33.3 (+), 0.2; 33.1 (◇), 0.4; 32.9 (○), 0.6; 32.7 (●), 1.0; 32.3 (×), 1.4; and 31.9 (△) mN m^{-1} for sunflower oil and γ_o^p; $\gamma_o^d = 0.9$; 19.9 mN m^{-1} for PDMS. Reproduced from ref 85 with permission from The Royal Society of Chemistry. (b) Microscopy image of multiple olive oil-in-100 cS PDMS oil-in-olive oil emulsions in which inner drops are stabilized by 20% SiOH hydrophobic silica and outer globules are stabilized by 70% SiOH more hydrophilic silica (left) and a sketch of the emulsion structure (right). Reprinted from *J. Colloid Interface Sci.* **2017**, *488*, 127. Copyright (2017) with permission from Elsevier.
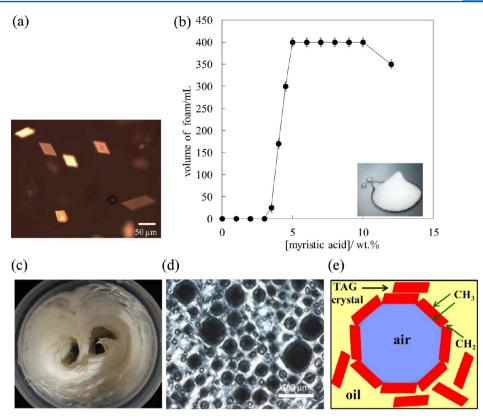
SiOH). They increase with an increase in the value of % SiOH (contrast for oil−water where they decrease) and with an increase in the magnitude of the polar contribution γ_o^p of the vegetable oil. The angles predict V/S emulsions (<90°) at low % SiOH and S/V emulsions (>90°) at high % SiOH as found experimentally. A value of $\gamma_o^p = 1.0$ mN/m for sunflower oil was necessary to predict the correct % SiOH at phase inversion where $\theta_{o1o2} = 90°$. It was also confirmed that a range of hydrophobic particles of different chemical type, size, and shape were efficient stabilizers of oil−oil emulsions.[85] Finally, by utilizing particle types of different hydrophobicities, stable multiple V/S/V emulsions can be prepared in two steps[88] in which more hydrophobic particles coat inner droplets and more hydrophilic particles coat outer globules (Figure 8b).

Air−Oil Surfaces. Oil (or nonaqueous) foams, a/o, are less common than aqueous foams but may occur during the use of lubricating oils[89] and in certain aerated fat-based confectionery such as chocolate. This is because the air−oil surface tension is typically around 20−35 mN m^{-1}, too low to drive the

adsorption of most solute species. Despite this, various hydrocarbon surfactants[90,91] and polymers[92] have been shown to temporarily stabilize oil foams, particularly under conditions close to a phase-separation boundary when the oil affinity for the solute is low. For particles to adsorb at the air−oil surface, particles are required to be of lower surface energy than those of hydrocarbon oils, and thus fluorocarbon (F)-containing particles offer this potential.[93] Using either commercial OTFE/PTFE particles[94] or fluorinated fumed silica particles[95] or fluorinated clay platelet particles,[96] we have systematically studied the effect of oil type and the extent of particle fluorination on foamability and foam stability including an estimation of the particle surface energy. In summary, an oil dispersion of particles forms in oils of low surface tension, e.g., silicone oil, with particles of low F content (oleophilic). Particle-stabilized oil foams, however, form both in systems of oils of higher tension (>32 mN m^{-1}, e.g., sunflower oil) and particles of intermediate F content and with oils of lower tension (to 27 mN m^{-1}, e.g., hexadecane) and particles of high F content. The foamability of the oils increases with particle concentration, and a majority of foams are stable to coalescence and disproportionation for over 6 months even though drainage occurs. Such foams can be seen in Figure 9a for a range of oils stabilized by quasi-spherical silica particles.[95] The foams are composed of relatively small bubbles (<100 μm) possessing textured surfaces, and many are nonspherical in

Figure 9. (a) Appearance of oil foams stabilized by 2 wt % fumed fluorosilica particles for (i) α-hexylcinnamaldehyde, (ii) α-bromonaphthalene, (iii) benzyl acetate, and (iv) eugenol. (b) Microscopy image of (iii), small scale bar = 100 μm. Reproduced from ref 95 with permission from The Royal Society of Chemistry. (c) Critical oil/particle ratio versus oil surface tension for a range of platelet fluorinated sericite clay particles of different extents of fluorination. (Inset) Schematic of an air-in-oil foam above the COPR and dry oil powder below COPR. (d) Photograph of dry liquid paraffin powder flowing through a glass funnel onto a watch glass (scale bar = 1 cm). Reproduced from ref 96 with permission from The Royal Society of Chemistry.
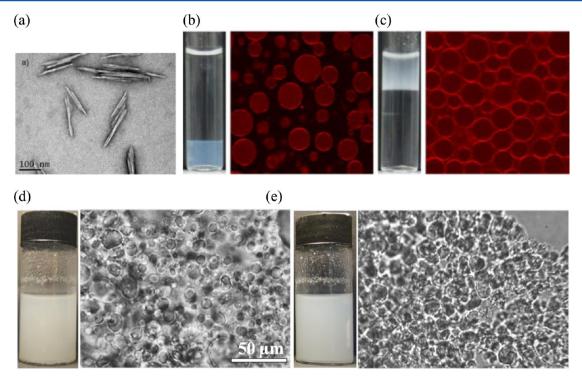
Figure 10. (a) Polarizing microscopy image of myristic acid crystals in HOSO at 22 °C. (b) Volume of the aerated phase produced after whipping 200 mL of a myristic acid−HOSO mixture at 22 °C versus [myristic acid]; the inset is a photograph of the oil foam at 8 wt % myrsitic acid. Reproduced from ref 99 with permission from The Royal Society of Chemistry. (c) Photograph from above during the whipping of coconut oil at 19 °C after 5 min. (d) Polarizing microscopy image of coconut oil foam formed at 23 °C after 24 h. (e) Schematic of the stabilization of an air bubble in oil by TAG crystals; methyl groups face both air and oil whereas methylene groups interact with neighboring adsorbed crystals. Reprinted from *Food Res. Int.* **2017**, *95*, 28. Copyright (2017) with permission from Elsevier.

shape (Figure 9b). Interestingly, for particle−oil combinations stabilizing foams, oil liquid marbles (o/a) can also be prepared, with the particles of highest F content encapsulating oils of lowest surface tension. In the case of fluorinated clay platelet microparticles, we discovered that dry oil powders in which oil drops are stabilized by particles dispersed in air (o/a) can be prepared by gentle mixing up to a critical oil/particle ratio (COPR).[96] Above the COPR, oil foams (a/o) form via catastrophic phase inversion such that the curvature of the air−oil surface is inverted (Figure 9c). The maximum amount of oil that can be incorporated into the oil powder increases with the F content of the particles and with the oil surface tension, γ_{la}. Oil powders shown in Figure 9d, containing up to 80 wt % oil, do not leak oil at rest but oil release can be effected when sheared on a substrate. We thus demonstrate that novel materials (foam, dry powder) can be produced in one and the same system simply by varying the overall composition. The findings were rationalized in terms of the air−oil−solid contact angles on planar substrates.[95,96]

A different strategy used recently to prepare stable oil foams from oil-soluble molecular surfactant has been to allow crystals of the additive to form within the oil phase on cooling, which, after aeration, adsorb to air bubble surfaces endowing the foam with high stability to drainage, coalescence, and disproportionation. These mixtures can be thought of as a high-melting-point additive (forms crystals) within a low-melting-point oil (continuous phase). In the four examples studied so far, the latter has been a vegetable oil with applications to aerated foods, but this is not a requirement. The systems have been a

commercial mono/diglyceride surfactant in rapeseed oil,[97] long-chain alcohols in sunflower oil,[98] a long-chain carboxylic acid in high oleic sunflower oil (HOSO) and other vegetable oils,[99] and a saturated triglyceride in a soybean oil−rapeseed oil mixture.[100] The oils above are examples of triacylglycerides (TAG) in which a high proportion of the long fatty acid chains are unsaturated such that the melting point of the oil is low (<0 °C) and hence the oils are liquid at room temperature. Thus, for example, a one-phase oil solution of myristic acid in HOSO forms at high temperature, which, on cooling below the solubility limit, produces a two-phase mixture of fatty acid crystals dispersed in an oil solution at its solubility.[99] It is proven that molecular fatty acid is not surface-active because no foam is possible in the one-phase region. The crystals are platelike (Figure 10a), and after whipping the oil, they coat the air bubbles in the foam. Very stable foams may be produced either by increasing the fatty acid concentration at fixed temperature (Figure 10b) or by aerating the mixtures at different temperatures at constant concentration. Excess fatty acid crystals serve to gel the continuous oil phase as in oleogels, enhancing the stability of the foam to drainage. Furthermore, these crystal-stabilized oil foams are temperature-sensitive, being rendered completely unstable on heating to around the melting temperature of the crystals. The findings were extended to a range of vegetable oil foams that are destabilized at different temperatures depending on the composition and type of fatty acid chains in the TAG molecules.[99] In a very recent study,[101] the possibility of creating stable, additive-free oil foams from an oil/fat containing a high proportion of saturated

Figure 11. Water-in-water emulsions stabilized by (a) labeled CNC particles (160 nm × 6 nm × 6 nm) at 0.5 g/L. (b) Photograph and microscopy image of a very unstable dextran-in-PEO emulsion, ϕ = 0.25. (c) Photograph and microscopy image of a stable PEO-in-dextran emulsion, ϕ = 0.33. Image dimensions are 160 μm × 160 μm. Reprinted with permission from *ACS MacroLett* **2016**, *5*, 283. Copyright (2016) American Chemical Society. Water-in-water emulsions stabilized by partially hydrophobic fumed silica particles at 2 wt % after 1 month at 20 °C. (d) Stable Na_2SO_4-in-PEO emulsion, ϕ = 0.2. (e) Stable PEO-in-Na_2SO_4 emulsion, ϕ = 0.3. Taken from ref 118.

medium-length fatty acid chains was reported. Because such oils are composed of a mixture of TAGs of different chain length/composition, we made use of the selective crystallization of those molecules of higher melting point within a liquid oil of those molecules of lower melting point. That is, an oil dispersion of crystals forms from one and the same oil. The majority of the study was devoted to coconut oil (mainly C_8–C_{16}), but similar findings were seen with shea butter and cocoa butter. For each oil, there exists an optimum temperature for foaming at which the solid fat content reaches around 30%. Figure 10c is a photograph of coconut oil after being whipped at 19 °C (melting point 25 °C), and Figure 10d is a polarizing microscopy image of the foam formed at 23 °C (optimum) where anisotropic TAG crystals can be evidenced mainly at air bubble surfaces but also within the continuous oil phase. The average bubble diameter at this temperature is around 30 μm, and no change in size is evidenced over a period of 2 months. On the basis of micro-X-ray diffraction of similar foams,[100] we suggested the arrangement of TAG crystals around air bubbles as sketched in Figure 10e. The lamellar planes (or faces) of the TAG crystals are aligned parallel to the air–oil surface but are randomly arranged within the oil phase. Because the surface energy of the faces composed of methyl groups is low, it is likely that they are in contact with air on one side and oil on the other, whereas the edges composed of higher-energy methylene groups and glycerol units interact with each other laterally through neighboring crystals adsorbed at the bubble surface. The study opens up the potential of creating reduced-fat-containing compositions in the absence of synthetic ingredients.

Water–Water Interfaces. Because of the trend toward sustainable ingredient sources, biodegradable products, and low-calorie food, there is a demand to develop completely water-based fluid systems. Aqueous solutions containing chemically distinct polymers exhibit phase separation above a certain concentration of each polymer (typically a few wt %). In these aqueous two-phase systems (ATPS),[102] the temperature, salt concentration, pH, and polymer molecular size all have an effect on phase separation. Many water-soluble polymers of industrial relevance exhibit phase separation, such as xanthan, maltodextrin, and poly(ethylene oxide), PEO. Systems particularly suitable for study form clear phases, do not contain aggregates, and do not gel. A popular example in this case is mixtures of dextran (a polysaccharide) and PEO. Segregative phase separation eventually results in the formation of macroscopic water phases, one rich in one polymer and the other rich in the other polymer, whose difference in density produces a two-layer system. Stirring or some other form of shear will disrupt the bulk phases into droplets, leading to a temporary water-in-water emulsion (w/w).[103] The water–water interface is characterized by an extremely low interfacial tension, typically 1 μN m^{-1}, which is a factor of 5 × 10^4 lower than that of an alkane–water interface. Because the density difference caused mainly by the difference in the water binding of the two polymers is typically 10^{-3} g cm^{-3} compared to that between an alkane and water of 0.3 g cm^{-3}, the achievement of complete phase separation of water–water mixtures may take days instead of minutes.[104] Because the interface is permeable to small ions and water and is much thicker (tens of nanometers) than that of the oil–water interface, all of these factors result in the difficulty of finding effective stabilizers of w/w emulsions. Many common surfactants whose molecules cannot straddle the interfacial zone are ineffective stabilizers, although certain triblock copolymers have been shown to

stabilize dextran–PEO emulsions for at least 6 months.[105] Interestingly, phospholipid liposomes of 130 nm diameter are also effective stabilizers and remain intact at the interface.[106] Oppositely charged polyelectrolytes (one in each aqueous phase) may also self-assemble at the water–water interface, forming PECs responsible for droplet stabilization,[107,108] although these systems now contain at least five components.

The option of using particles as the emulsifier of water–water emulsions has been considered recently. For spherical particles with $\theta = 90°$, an adsorption energy of $20kT$ requires particles of at least 160 nm in radius if the interfacial tension is 1 μN m^{-1}. The adsorption energy of a platelet particle, whose preferential orientation is parallel to the interface, is greater than that of a sphere at all angles other than 90°. In several studies to date involving two polymers, the particles have included fat or protein,[109] polystyrene,[110] protein,[111−113] polymer microgel,[114] gibbsite plates ($Al(OH)_3$),[115] and cellulose rods.[116] Unlike the case of oil–water emulsions, the role of particle wettability and particle size is unclear at present in these emulsions. As an example, Figure 11 from the work of Peddireddy et al.[116] shows the use of rodlike particles of cellulose nanocrystals (CNC, (a)) in dextran (lower)–PEO (upper) mixtures. Denoting ϕ as the volume fraction of the dispersed phase, a very unstable dextran-in-PEO emulsion results when ϕ = 0.25 (b), whereas a very stable PEO-in-dextran emulsion forms when ϕ = 0.33 (c). Many questions remain in this area, including whether one or both polymers adsorbs on particle surfaces and the impact this has on their adsorption to the water–water interface. In an attempt to simplify the system, we decided to investigate systems involving only one polymer (PEO) that phase separates in the presence of certain salts.[117] At room temperature, aqueous solutions of PEO of molecular weight 8000 and Na_2SO_4 demix with the volume fraction of the lower salt-rich phase increasing with salt concentration.[118] No stable emulsion could be prepared for ϕ = 0.5 with common anionic, cationic, or nonionic surfactants at up to 20 times their critical micelle concentrations. However, emulsions stable to coalescence for at least 1 month can be prepared in the presence of 2 wt % fumed silica particles of intermediate hydrophobicity. As seen in Figure 11d, a Na_2SO_4-in-PEO emulsion is preferred at ϕ = 0.2, which does not sediment. Likewise, a PEO-in-Na_2SO_4 emulsion is preferred at ϕ = 0.3, which shows evidence of creaming, yielding a more concentrated emulsion (Figure 11e). The average drop diameter in both emulsion types is relatively small, ca. 20 μm.

CONCLUSIONS AND OUTLOOK

It can be seen that research in the area of colloidal particles at liquid interfaces is very active, particularly by experimentalists. Many kinds of particle can be synthesized, differing in chemistry, size, and shape such that particle–interface and particle–particle interactions can be modulated using existing colloid science principles. New materials whose stability is dominated by the irreversible adsorption of interfacial particles are emerging. In some cases, multiple interfaces are present between liquid and vapor and liquid and liquid. Although surfactant-free formulations such as foams and emulsions are of interest to industrialists, the development of new products by companies has been slow, although several patents have been filed. It is fair to say that theoretical and simulation efforts have also lagged behind experimental progress. Future research in our opinion should concentrate on (i) mixtures of particles differing in size, wettability, chemical type, and shape; (ii)

particle–surfactant mixtures for cases in which surfactant adsorbs on particle surfaces and for those in which it does not; (iii) water-free emulsions in which water is replaced by another polar solvent or an immiscible oil; (iv) the simultaneous use of particles as both an emulsion and foam stabilizer and as a catalyst or active ingredient in, for example, a sunscreen formulation; and (v) the elucidation of the role of interfacial rheology in the properties and stability of particle-stabilized materials.

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The author declares no competing financial interest.

Biography

Bernard P. Binks obtained his B.Sc. in chemistry (1983) and a Ph.D. in surface chemistry and microemulsions (1986) at the University of Hull, U.K. He was awarded a Royal Society European Fellowship to study in Paris, where he worked on light scattering and ellipsometry from liquid interfaces coated with surfactant (1987). After further postdoctoral years studying Langmuir monolayers on water and multilayers on solid substrates, he was appointed Lecturer in Chemistry at the University of Hull in 1991. He was promoted to Professor of Physical Chemistry in 2003 and has led the Surfactant & Colloid Group at Hull since 2002. His main research interests are in the properties and behavior of colloidal particles at fluid interfaces, including particles at planar interfaces, particle-stabilized emulsions and foams, and novel materials derived from them. He has published over 260 peer-reviewed articles and 13 patents and has edited 3 research monographs. He was awarded the RSC Colloid & Interface Science Group medal in 2004, the European Colloid and Interface Society-Rhodia Prize in 2011, the RSC Surfaces and Interfaces Award in 2014, and the ACS Langmuir Lectureship in 2016. He is currently a Senior Editor of Langmuir.

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