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Emulsions

Double Inversion of Emulsions By Using Nanoparticles and a Di-Chain Surfactant**

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The use of surfactant molecules as emulsifiers of oil and water has been extensively studied in the past. However, only recently has a thorough understanding of emulsion stabilization by solid particles alone been achieved.[1] Colloidal particles, like surfactant molecules, can be surface active and will spontaneously adsorb at the interface of two immiscible liquids. Such particles readily form very stable emulsions, which have been used as templates to allow the preparation of, for example, hollow capsules[2] and nanotubosomes.[3] However, as many commercial formulations contain a mixture of particles and surfactants, understanding how they interact is crucial. Although the single phase inversion of emulsions from oil-in-water (o/w) to water-in-oil (w/o) emulsions or vice versa can be achieved with particles or surfactant alone, for example, by changing the particle hydrophobicity,[4] temperature,[5] or salt concentration,[6] to the best of our knowledge no example of double phase inversion exists. Herein, we report how, by suitable choice of a nanoparticle–surfactant mixture of opposite charge, emulsions can be inverted initially from o/w to w/o and subsequently back to o/w upon increasing the surfactant concentration. The adsorption of surfactant onto particle surfaces contributes to the origin of this double inversion.

One key parameter controlling the type and stability of solid-stabilized emulsions is the wettability of the particles attached to the oil–water interface.[1] Particles of intermediate wettability were shown to be the most effective emulsifiers.[4] For very hydrophilic particles, which are poor emulsifiers alone, the addition of a surfactant that adsorbs on particle surfaces through their hydrophilic head groups modifies their wettability resulting in an improvement of emulsion stability.[7] In some cases, particles were rendered sufficiently hydrophobic to cause single emulsion phase inversion from o/w to w/o.[8,9] This is due to the formation of a surfactant monolayer on particle surfaces leaving surfactant chains exposed to water and thus increasing the hydrophobicity of the particles. The examples quoted above were for various inorganic micron-sized particles in the presence of single-chain surfactants. By choosing a di-chain cationic surfactant in mixtures with negatively charged silica nanoparticles, it is possible to effect a second emulsion phase inversion from w/o to o/w at higher surfactant concentration. We postulate that formation of a surfactant bilayer on particle surfaces renders the particles hydrophilic again such that they prefer to stabilize o/w emulsions.

The interactions between oppositely charged surfactant molecules and silica particles in water enable us to understand the synergistic behavior that they display in stabilizing emulsions. At relatively high pH values, silica nanoparticles of a diameter of 15 nm are negatively charged, of high charge density, and are stable as aqueous dispersions. At a fixed particle concentration (2 wt %), the addition of the di-chain cationic surfactant didecyldimethylammonium bromide (di-C_{10}DMAB) induces destabilization of the dispersions at low concentration values followed by restabilization at higher concentrations. As seen in Figure 1, surfactant addition causes particle flocculation leading to their sedimentation,[10] with the extent of sedimentation passing through a maximum. Sedimentation is initiated at an initial surfactant concentration close to the critical micelle concentration (cmc) of 1.8 mM. The cmc was determined here from interfacial tension measurements and was found to be in agreement with a literature value.[11]

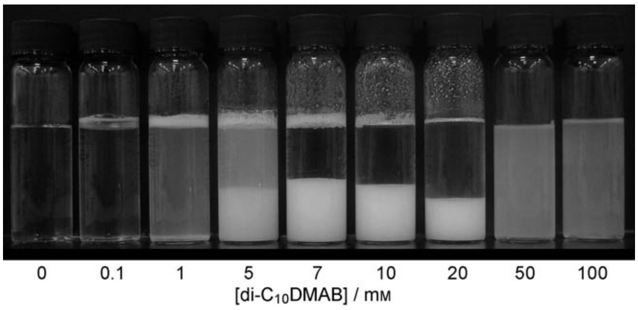

Figure 1. The appearance after 24 h of aqueous dispersions of 2 wt% Ludox HS-30 silica nanoparticles as a function of initial di-C_{10}DMAB surfactant concentration (given in mM) at 20 °C and high pH. Stable dispersions initially flocculate and sediment followed by redispersion.

The origin of particle flocculation is the adsorption of positively charged surfactant on negatively charged silica particles, which partially screens the repulsion between the particles in addition to increasing their hydrophobicity. The former can be monitored by following the change in the particle zeta potential upon surfactant addition. In the absence of surfactant, the zeta potential of silica particles is -42 mV at their natural pH value of 9.8. Figure 2 shows the

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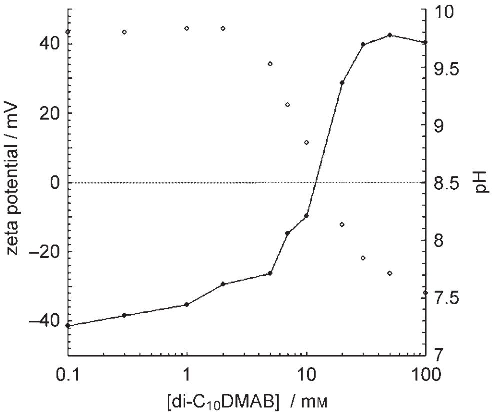

Figure 2. Zeta potential (◆) and pH values (◇) of 2 wt% Ludox HS-30 aqueous silica dispersions as a function of the initial di-C$_{10}$DMAB surfactant concentration at 20 °C.

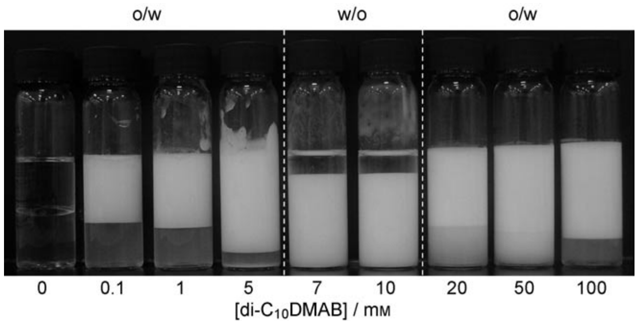

Figure 3. The appearance after 24 h of dodecane–water emulsions (1:1 by volume) stabilized by a mixture of 2 wt% Ludox HS-30 silica nanoparticles and di-C$_{10}$DMAB surfactant at different initial concentrations (given in mM). Emulsions invert from o/w to w/o and back to o/w from left to right. Note the creaming for o/w emulsions, the sedimentation for w/o emulsions, and no coalescence observed in the mixtures.

influence of surfactant concentration on both the zeta potential and the pH value of the aqueous dispersions. The magnitude of the negative zeta potential (◆) decreases gently at low surfactant concentrations and then more markedly at higher concentrations, passing through a zero value at around 12 mM and becoming increasingly positive thereafter. This charge reversal is due to the formation initially of an adsorbed surfactant monolayer on particles (neutralizing the charged silanol groups) followed by the formation of a surfactant bilayer exposing head groups to the continuous aqueous phase.[12] The positively charged bilayer-coated particles are repulsive leading to restabilization of the dispersion. The final pH value of aqueous dispersions (◇) is governed by the extent of adsorption onto particle surfaces. Up to the cmc, the pH value remains constant at around 9.8. Above the cmc, it gradually decreases to 7.5 as loss of surfactant to particles further drives the dissociation of silanol groups (SiOH), liberating free protons in solution. As shown theoretically,[13] solid surfaces are most hydrophobic at conditions of zero charge. Thus, it is expected that with increasing surfactant concentration, particles that are initially hydrophilic become hydrophobic near the isoelectric point where they flocculate the most and then hydrophilic again once recharged.

Following the above, it is predicted that emulsions prepared from mixtures of silica particles and di-chain cationic surfactant will progress from o/w to w/o and to o/w again on increasing the surfactant concentration. In the case of emulsions containing equal volumes of dodecane and water with a single emulsifier, the silica-particle-stabilized system phase separates completely after formation as highly charged hydrophilic silica is a poor emulsifier[4] (see the far left vessel in Figure 3). In contrast, the surfactant-stabilized system yields o/w emulsions whose stability to coalescence increases progressively with concentration, although they exhibit creaming with time. A series of emulsions prepared from the mixed aqueous dispersions shown in Figure 1 was prepared at 20 °C. In Figure 3, the type and stability of these emulsions are immediately obvious. Up to 5 mM surfactant, emulsions are o/w, which cream, leaving a serum below. At 7 and 10 mM surfactant, w/o emulsions form and the resulting emulsion drops sediment with time, leaving a clear supernatant oil phase. Finally, above 20 mM surfactant, emulsions are o/w again and exhibit creaming. The double phase inversion observed is supported both by drop tests and by comparing the emulsion conductivities as given in Table 1. The latter are high at low surfactant concentration, fall to low values at intermediate concentration (consistent with oil as the continuous phase), and increase to high values again as water becomes the new continuous phase. Emulsions formed from particle–surfactant mixtures are gel-like and stable to coalescence indefinitely compared with those of surfactant alone, which are more fluid and liberate free oil after long times. This synergistic stabilization is advantageous.

Table 1: Effect of initial surfactant concentration on the conductivity (κ) and median drop diameter (*d*) of 1:1 emulsions of dodecane and 2 wt% aqueous Ludox HS-30 silica nanoparticles at high pH.

di-C$_{10}$DMAB [mM]	κ [μS cm^{-1}]	*d* [μm]
0.1	206	66
1	250	67
5	266	55
7	2	42[a]
10	2	33[a]
20	202	10
50	552	6
100	832	4

[a] Average of 50 spherical water drops by optical microscopy.

The appearance of the drops in the different types of emulsion has been probed by microscopy. In Figure 4, oil drops at low and high surfactant concentration (a,c) are spherical and discrete. However, some of the water drops at an intermediate concentration (b) are nonspherical and appear flocculated. It can be seen that there is a gradual decrease in the average drop diameter with increasing surfactant concentration (Table 1). From the adsorption isotherm in aqueous dispersions, the amount of surfactant lost to particle surfaces decreases from 97% to 57% on increasing the initial surfactant concentration from 7 to 30 mM. Hence, the decrease in drop size may be due to the

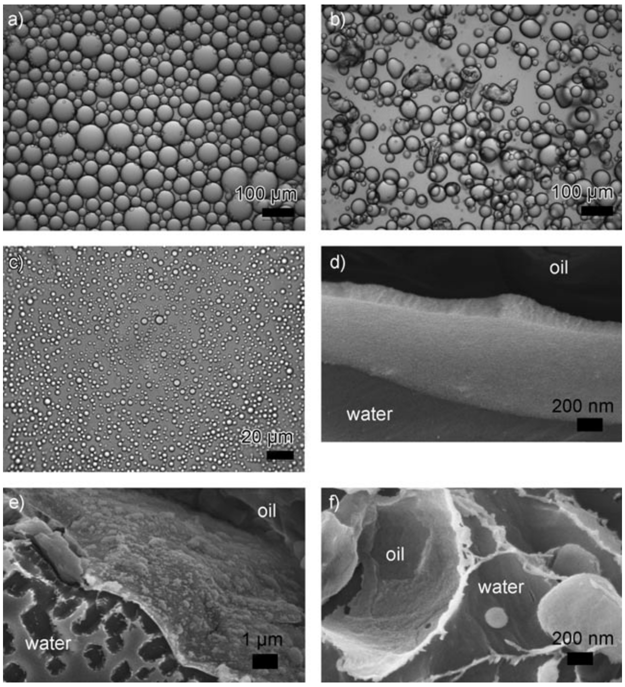

Figure 4. Optical microscopy images of different types of dodecane–water (1:1) emulsions obtained during the double phase inversion induced by increasing surfactant concentration. a) o/w at 0.1 mM, b) w/o at 7 mM, and c) o/w at 100 mM. Cryo-SEM images showing the interfacial arrangement of particles for d) an oil drop at 1 mM, e) a water drop at 7 mM, and f) an oil drop at 50 mM.

adsorption of free surfactant at the oil–water interface, lowering its tension and promoting emulsification. The arrangement of particles around droplets has also been probed by using cryogenic-scanning electron microscopy (cryo-SEM). The interfacial layer, which has a thickness greater than 100 nm encapsulating an oil drop, is composed of close-packed particles layered in more than a monolayer (Figure 4d). For w/o emulsions (Figure 4e), the flocculated particles originally present in the aqueous phase appear to have adsorbed on water drop interfaces, and interfacial regions devoid of such flocs are also present. The average floc size is a few hundred nanometers. The existence of a network of flocculated particles is also evident within the water drops. Finally, for o/w emulsions at high surfactant concentrations (Figure 4f), the interface is covered with close-packed particles and the continuous aqueous phase contains either aggregated excess surfactant (white object) probably in the form of vesicles[14] or ice crystal artifacts.

The effect of surfactant on the wettability of silica in relation to the emulsion type has been investigated on planar silicon wafer surfaces at high pH values. In these experiments, the aqueous phase contacted the solid first before a captive oil drop was released below the surface. The contact angles measured through the aqueous phase increase from 51° without surfactant to 165° for 1 mM surfactant and then decrease to very low values (< 5°) with 10 mM surfactant, that is, the originally hydrophilic surfaces become very hydrophobic and then hydrophilic again in line with the double emulsion phase inversion. The surfactant concentrations mentioned above do not coincide with those in Figure 3 as both the oil:water ratio and the solid surface area are vastly different in the two cases. The structure of the surfactant is crucial in dictating whether emulsion inversion occurs or not. Thus, although the single-chain cationic surfactant hexadecyltrimethylammonium bromide adsorbs on silica particle surfaces as is the case here for the di-chain analogue, particles do not become hydrophobic enough to stabilize w/o emulsions and the maximum contact angle reached was only 110°.[7] By contrast, the di-chain surfactant induces sufficient hydrophobicity to enable inversion to w/o emulsions. The reason for this difference is associated with the extent of packing of surfactant molecules on surfaces. From the adsorption isotherms of cationic surfactants on silica particles, Esumi et al.[15] conclude that the di-chain surfactant is more closely packed than the corresponding single-chain surfactant of the same chain length. At saturation, the areas per chain are 0.23 and 0.35 nm^2, respectively. The enhanced packing of the di-chain surfactant within a monolayer on particle surfaces results in a more hydrophobic surface. The origin of the second inversion is not clear at present; it may be driven by adsorption of the hydrophilic surfactant-coated particles or dominated by that of free surfactant or a combination of the two.

To conclude, we report the double phase inversion of emulsions stabilized by a mixture of silica nanoparticles and di-chain cationic surfactant induced by surfactant concentration alone. The first inversion from o/w to w/o is linked to the flocculation of particles by the surfactant owing to the particles becoming hydrophobic through monolayer adsorption. The subsequent inversion from w/o to o/w occurs as particles are deflocculated and become highly charged again through formation of a surfactant bilayer. This novel double phase inversion offers the potential of selecting the emulsion type easily for a particular application.

Experimental Section

Monodisperse silica particles (Ludox HS-30) were purchased from Grace Davison as an aqueous dispersion (31.6 wt %) at pH 9.8. The average particle diameter is 15 nm, which was determined by TEM and dynamic light scattering.[7] The specific surface area is 220 m^2 g^{-1}. Didecyldimethylammonium bromide surfactant, di-C$_{10}$DMAB, of a purity greater than 98 % was from Tokyo Chemical Industry Co. *n*-Dodecane (99 %, Aldrich) was filtered by column chromatography twice through basic alumina to remove polar impurities. Water was first passed through an Elga reverse osmosis unit and then a Milli-Q reagent water system. Aqueous dispersions of 2 wt % silica particles were prepared in solutions of surfactant without adjusting the pH value. The pH value was measured by using a FisherBrand Hydrus 400 fitted with a glass combination electrode. The stability of dispersions at 20 °C was determined by measuring the height of the sediment after 24 h. The zeta potential distributions of silica particles were obtained at 20 °C by using a Malvern Zetasizer 3000HS. The supernatant was used for sedimented samples. Batch emulsions of 10 mL containing equal volumes of dodecane and aqueous dispersions containing the particles and surfactant were prepared at 20 °C by using an IKA Ultra Turrax T25 homogenizer with a 0.8-cm head operating at 11 000 rpm for 1 min. Immediately after emulsification, the emulsion type was determined by a drop test and by conductivity with a Jenway 4510 conductivity meter with an epoxy body cell. The stability of emulsions to creaming, sedimentation, and coalescence was assessed by monitoring the heights of resolved water and oil from the emulsion phase over time. Photographs of vessels were taken by using a Canon IXUS55 digital camera. Drops of diluted emulsions were imaged with a Nikon Labophot microscope fitted with a digital camera QICAM 12-bit mono Fast 1394 (QImaging) and by using Image-Pro Plus 5.1 software (Media Cybernetics). Drop size distributions were obtained by light diffraction of a diluted emulsion by using a Malvern Mastersizer 2000. Cryo-SEM images were obtained at −150 °C by using a JEOL 6301F scanning electron microscope. Samples were initially frozen with liquid nitrogen, fractured at −97 °C with a scalpel, and then coated with a Pt/Pd alloy at −110 °C. The contact angles of captive dodecane drops (20 μL) under an aqueous surfactant solution at pH 9.5 on a hydrophilic silicon wafer were determined by using a Krüss DSA10 instrument. The oil–water interfacial tension was measured at 20 °C with the same instrument by using a pendant aqueous drop in oil.

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[1] *Colloidal Particles at Liquid Interfaces* (Eds.: B. P. Binks, T. S. Horozov), Cambridge University Press, Cambridge, **2006**, 1 – 74.
[2] A. D. Dinsmore, M. F. Hsu, M. G. Nikolaides, M. Marquez, A. R. Bausch, D. A. Weitz, *Science* **2002**, *298*, 1006 – 1009.
[3] M. in het Panhuis, V. N. Paunov, *Chem. Commun.* **2005**, 1726 – 1728.
[4] B. P. Binks, S. O. Lumsdon, *Langmuir* **2000**, *16*, 8622 – 8631.
[5] K. Shinoda, H. Saito, *J. Colloid Interface Sci.* **1969**, *30*, 258 – 263.
[6] B. P. Binks, *Colloids Surf. A* **1993**, *71*, 167 – 172.
[7] B. P. Binks, J. A. Rodrigues, W. J. Frith, *Langmuir* **2007**, *23*, 3626 – 3636.
[8] J. H. Schulman, J. Leja, *Trans. Faraday Soc.* **1954**, *50*, 598 – 605.
[9] D. E. Tambe, M. M. Sharma, *J. Colloid Interface Sci.* **1993**, *157*, 244 – 253.
[10] H. Hassander, B. Johansson, B. Törnell, *Colloids Surf.* **1989**, *40*, 93 – 105.
[11] P. Lianos, J. Lang, R. Zana, *J. Colloid Interface Sci.* **1983**, *91*, 276 – 279.
[12] R. Atkin, V. S. J. Craig, E. J. Wanless, S. Biggs, *Adv. Colloid Interface Sci.* **2003**, *103*, 219 – 304.
[13] L. G. J. Fokkink, J. Ralston, *Colloids Surf.* **1989**, *36*, 69 – 76.
[14] E. Junquera, P. del Burgo, J. Boskovic, E. Aicart, *Langmuir* **2005**, *21*, 7143 – 7152.
[15] K. Esumi, M. Matoba, Y. Yamanaka, *Langmuir* **1996**, *12*, 2130 – 2135.