Colloids

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Particle-Stabilized Emulsions: A Bilayer or a Bridging Monolayer?**

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Solid colloidal particles are widely used in many industries, for example, food, cosmetics, paper, paint etc. The fact that they can be irreversibly held at fluid interfaces and stabilize emulsions was realized a long time ago.[1,2] Recently, it was shown that certain solid nanoparticles alone can act as excellent emulsion[3–5] and foam stabilizers.[3,6] It is accepted that the stability of particle-stabilized emulsions is due to the coherent particle layer around the droplets, which acts as a steric (mechanical) barrier against coalescence.[3,7,8] This situation implies that particle interactions at the droplet surface are dominated by attractive forces, which results in the formation of coherent monolayers with significant mechanical strength.[7,8] Recent results have shown that stable emulsions can be formed even if the droplets are barely covered with well-separated particles.[4] However, this does not fit in with the steric barrier mechanism of stabilization and is still enigmatic. Here, we demonstrate for the first time the link between particle behavior and interactions in planar monolayers and the mechanisms of emulsion stabilization. We show why strongly repulsive colloidal particles, which give well-ordered, dilute planar monolayers, can act as very effective emulsion stabilizers. This effect arises from the spontaneous accumulation of particles in a dense monolayer bridging the emulsion droplets sparsely covered with particles, thus preventing coalescence, as revealed by direct in situ microscope observations. Our results imply that two general mechanisms of emulsion stabilization by solid particles thus exist: 1) steric stabilization of emulsion droplets covered by coherent particle layers, and 2) stabilization by particle bridges when the droplets are sparsely covered. This is very important for understanding the fundamentals of solid-stabilized emulsions and designing more efficient particle stabilizers.

Small solid particles can spontaneously attach to air–water or oil–water interfaces to form monolayers. The energy needed for their detachment is usually much greater than the thermal energy; therefore they are irreversibly trapped at the fluid interface.[3] This effect determines the ability of certain colloidal particles to act as very effective emulsion and foam stabilizers.[3–8] In particle-stabilized emulsions, liquid droplets covered with coherent particle layers are dispersed in another immiscible liquid. The particle layers at the drop surface provide steric (mechanical) hindrance to droplet coalescence, thus making these emulsions completely stable for years.[3,7] This well-accepted mechanism of stabilization can be realized if the droplets are covered with sufficiently dense particle layers close to complete surface coverage[7] or if a rigid crust of particles forms around the droplets.[9] Some results, however, do not fit into this picture of emulsion stabilization. For example, Midmore has obtained very stable emulsions even though the estimated coverage of the droplets with silica nanoparticles was as low as around 29 %.[8] Recently, Vignati et al.[4] have reported stable emulsions at about 5 % particle coverage of the droplets, which cannot be explained by steric stabilization. On the basis of microscopy observations performed after dilution of the emulsions, they hypothesized that particles within the contact region may form a monolayer bridging the droplets, thus keeping them at a finite distance, which stabilizes the thin liquid film between the droplets and prevents coalescence.[4] The formation of bridging particle monolayers in isolated liquid films has been reported,[10–12] but direct experimental evidence of their existence in real emulsions is still missing. Hence, the mechanism of stabilization of emulsion droplets sparsely covered with particles remains unclear and enigmatic. This raised the question about the link between the structure of isolated particle monolayers

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and the mechanism of stabilization in particle-stabilized emulsions. Despite existing theoretical analyses,[7] such a link has not been shown experimentally until now.

Herein we report experimental results that demonstrate, for the first time, the link between the structure of planar monolayers of particles and the mechanism of stabilization of particle-stabilized emulsions. Planar monolayers of micrometer-size silica particles hydrophobized to different extents were formed at an octane–water interface and studied by microscopy. Slightly hydrophobic particles with a contact angle θ of 65° measured through the aqueous layer give aggregated disordered monolayers (Figure 1 a). In contrast, very hydrophobic particles with $\theta = 152°$ give monolayers with a totally different structure (Figure 1 b). The silica particles in the latter case are ordered in a hexagonal array at very large interparticle distances of around 50 μm. These results are consistent with our previous findings concerning the effect of particle hydrophobicity on particle interactions at oil–water interfaces.[13] The weak repulsion between less-hydrophobic particles ($\theta = 65°$) is insufficient to oppose the attraction; therefore, the particles easily aggregate and give disordered monolayers at very low electrolyte concentrations in the aqueous phase (10 mM NaCl). In contrast, the interactions between the most-hydrophobic silica particles ($\theta = 152°$) are dominated by strong, long-range Coulomb repulsion through the oil as a result of charges at the particle–oil interface. This finding is supported by the fact that these particles form well-ordered, stable monolayers with a crystalline structure even at high electrolyte concentration in the aqueous phase (100 mM). The reasons for such a remarkable difference in interactions between particles with different hydrophobicities have been analyzed elsewhere.[13] The question of interest here is whether the observed differences in the monolayer structure affect the way in which particles stabilize emulsions.

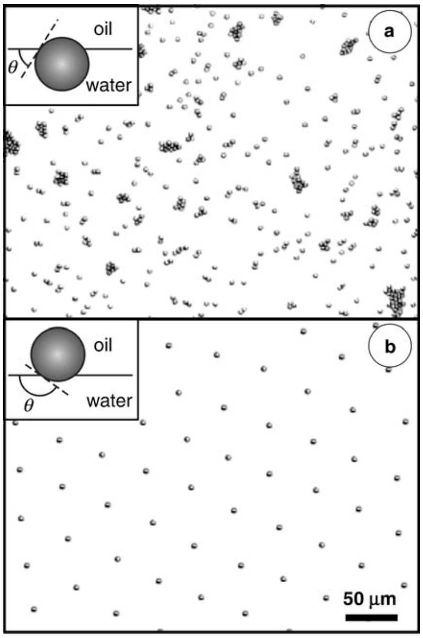

Figure 1. Images of horizontal, planar monolayers of silica particles at an octane–water interface 1 h after their formation by spreading. The particle diameter is 3 μm and particle contact angles θ are a) 65° and b) 152° (see insets). The aqueous phase contains 10 and 100 mM NaCl, respectively.

To answer the above question we studied emulsions formed by shaking equal volumes of octane and water in the presence of 1 wt% silica particles with different hydrophobicities to those used in the monolayer experiments. We found that an oil-in-water (o/w) emulsion is formed in the presence of less-hydrophobic particles ($\theta = 65°$), whereas a water-in-oil (w/o) emulsion is obtained when the most-hydrophobic particles ($\theta = 152°$) are used. This result is in agreement with previous findings that particles with $\theta < 90°$ can stabilize o/w emulsions, while those with $\theta > 90°$ give w/o emulsions.[2,3,5,7] In both cases the emulsions were unstable just after their formation, and fast creaming of the oil droplets in the o/w emulsion and sedimentation of the water droplets in the w/o emulsion was observed. The respective resolved bulk liquids were very clear, thereby suggesting that almost all the particles are adsorbed at the oil–water interface. This process was accompanied by very fast droplet coalescence during the first 10 s, but gradually slowed down, and after several minutes terminated completely. Further changes in droplet size were not detected and the emulsions were stable against coalescence for several months. This gradual transformation of an initially unstable emulsion into an indefinitely stable one is called a limited coalescence and is typical for particle-stabilized emulsions at low particle concentrations.[14]

Images of o/w and w/o emulsions taken in situ with a horizontal microscope about one hour after their formation are shown in Figure 2. Although the composition of both

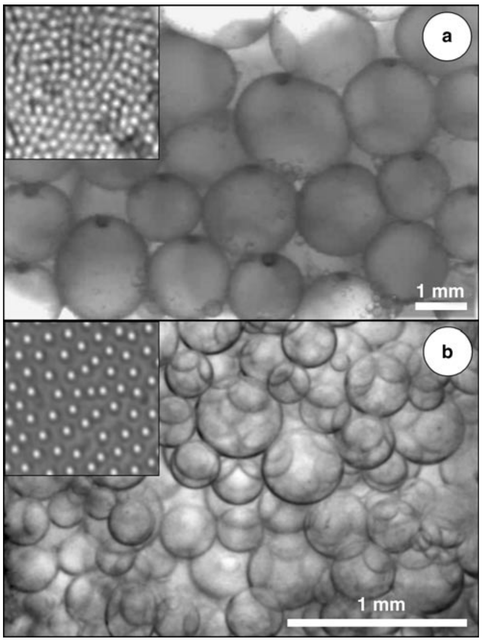

Figure 2. Images of a) an octane-in-water emulsion stabilized by slightly hydrophobic silica particles with a contact angle of 65° and b) a water-in-octane emulsion stabilized by very hydrophobic silica particles with a contact angle of 152°, both taken 1 h after emulsification by shaking. The particle diameter is 3 μm and particle concentration is 1% w/v. The insets (40×40 μm^2) show the monolayer structure in situ at the drop surface obtained at higher magnification.

emulsions is the same, the droplet size is remarkably different. The average diameter of oil droplets determined from the images of the stable o/w emulsion is 1.7 ± 0.2 mm (a), while that of the water droplets in the w/o emulsion is 0.3 ± 0.1 mm (b). Hence, the emulsion droplets stabilized by the most-hydrophobic particles are more than five times smaller than those stabilized by the less-hydrophobic ones. A closer look at the droplet surface at higher magnification reveals another interesting difference, namely that the oil droplets are covered with a dense monolayer of close-packed particles (a, inset), which can act as a steric barrier between the droplets and thus prevent coalescence. Surprisingly, the monolayers of the most-hydrophobic particles on the water droplets are rather dilute (b, inset). Although not perfectly ordered, as in the planar monolayers, the particles are well separated at around 6 µm (ca. two particle diameters). Clearly, these dilute particle monolayers cannot serve as a steric barrier against droplet coalescence, therefore there must be another reason for the prolonged stability of these emulsions.

The magnified in situ images of the w/o emulsion in Figure 3 solve the mystery. Several touching drops are shown in Figure 3 a. The circular contact regions (liquid films) between the drops are easily seen as bright spots marked "F". Their structure becomes clear at even higher magnification (Figure 3 b), where it can be seen that particles in the oil film between touching water droplets are well ordered in a dense disk with a crystalline structure. Spontaneous formation of similar crystalline disks of bridging particles has previously been observed during thinning of isolated oil films in water when the film surfaces were covered with dilute monolayers of very hydrophobic silica particles.[12] The same should happen when two droplets in the w/o emulsion come into contact: some of the particles become attached to the surface of both water droplets, thus forming stable particle bridges through the oil because θ is greater than 90°. One can conclude that the crystalline disks between touching droplets are, in fact, particle monolayers bridging the droplets. The significant particle density of the bridging monolayer is due to the strong capillary attraction between particles caused by the deformed menisci around them. The dense bridging monolayer ("F" in Figure 3 b) stabilizes the liquid film between droplets,[15] thus preventing coalescence, although the droplets are barely covered with particles outside the contact region ("D" in Figure 3 b). Therefore, the most-hydrophobic particles can form an emulsion with smaller drops and a larger interfacial area at the same adsorbed amount than that of the less-hydrophobic particles, which have to be closely packed at the drop surface to prevent coalescence.

Our results clearly show that there is a link between the particle interactions, the structure of their dilute planar monolayers, and the mechanism of emulsion stabilization. The lack of long-range repulsion between less-hydrophobic particles ($\theta = 65°$) results in the disordered structure of their dilute monolayers. For the same reason, these particles are easily dragged away from the central, thinnest part of isolated water films in oil and are unable to provide effective film stabilization.[12] Dense, close-packed monolayers are needed for film stabilization[12] and for protection of the emulsion droplets from coalescence (Figure 2 a). Hence, these emulsions are stabilized by the steric-hindrance mechanism (Figure 4 a). In contrast, the strong Coulomb repulsion

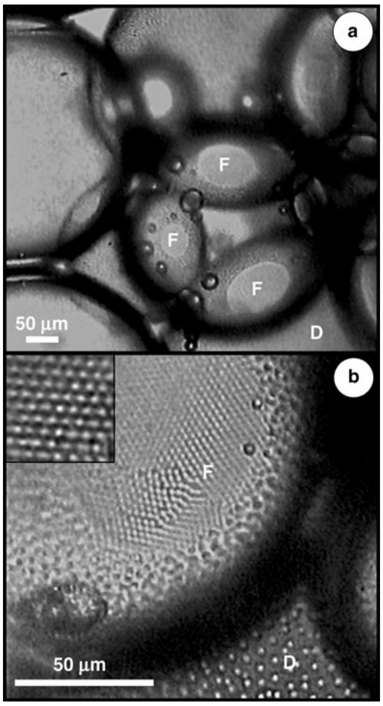

Figure 3. Images of the same water-in-octane emulsion as Figure 2 b at a) intermediate and b) higher magnification. The oil films (F) formed between touching water droplets are stabilized by dense, ordered monolayers of bridging particles (b, inset). The particles on the droplet surface outside the films (D) are well separated. The inset corresponds to an area of 25 × 25 µm^2.

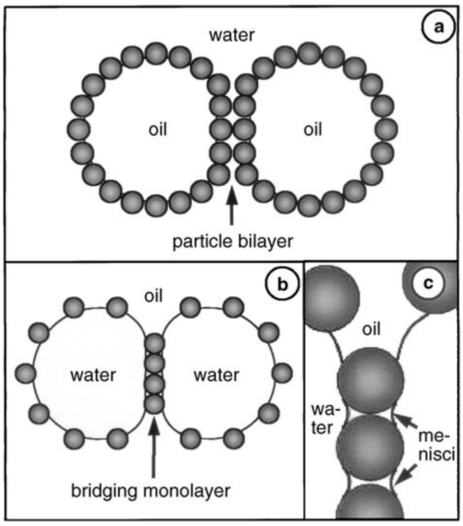

Figure 4. Two mechanisms of emulsion stabilization by colloidal particles: a) steric stabilization of emulsion droplets covered with dense, particle monolayers, and b) bridging stabilization of emulsion droplets covered with dilute particle monolayers. The particles on the emulsion droplets in the contact region form a dense, bridging monolayer as a result of strong capillary attraction caused by the menisci around them (c).

between the most-hydrophobic particles ($\theta = 152°$) results in the well-ordered structure of their monolayers (Figure 1 b). This repulsion keeps these particles in the thinnest region of isolated oil films in water, where they are able to bridge the film surfaces and to spontaneously form a dense, crystalline disk which prevents film rupture.[12] The same process occurs in the w/o emulsion during collisions between water droplets and effectively prevents them from coalescing even though the droplet surface is only partially covered with particles (Figure 2 b and Figure 3 b). Hence, these emulsions are stabilized by the bridging particle monolayer mechanism (Figure 4 b,c). This mechanism could explain some of the existing experimental data for high stability of emulsions at a low surface concentration of particles.[4,8,9]

The link between particle behavior and interactions in planar monolayers and the mechanism of emulsion stabilization by solid colloidal particles is clearly demonstrated by these experiments. Slightly hydrophobic silica particles, which give aggregated, disordered, planar monolayers as a consequence of the lack of strong interparticle repulsion, can stabilize emulsions by forming dense, close-packed monolayers at the droplet surface that act as a steric barrier against coalescence. In contrast, strongly repulsive colloidal particles, which give well-ordered, dilute, planar monolayers, can stabilize emulsions as a result of spontaneous particle accumulation in a dense monolayer bridging the emulsion droplets sparsely covered with particles. These findings are important for understanding the fundamentals of particle-stabilized emulsions. They will also help in designing more effective particle stabilizers by tuning the interactions between colloidal particles in planar monolayers at oil–water interfaces.

Experimental Section

Monodisperse silica particles of diameter 3.00 ± 0.05 μm and density 2 g cm^{-3} were purchased from Tokuyama Corp., Japan. They were hydrophobized to different extents with silanizing agents and the contact angles were determined as described elsewhere.[12] *n*-Octane (99 %, Lancaster) was passed several times through basic alumina (BDH) to remove polar impurities. Water was passed through a reverse osmosis unit and then a Milli-Q reagent system. The NaCl used had a purity of 99.9 % (from BDH). Planar monolayers of particles were formed by spreading a dilute particle suspension in 70 wt % 2-propanol/water at the octane–water interface in a small petri dish and were observed from above with a microscope, as described previously.[12,13] Emulsions were formed in glass cuvettes ($10 \times 10 \times 45$ mm^3, Helma) with teflon stoppers by mixing equal volumes of octane and water with silica particles. Before mixing, the less-hydrophobic particles were dispersed in water, whereas the most-hydrophobic ones were dispersed in octane. The cuvettes were then shaken vigorously by hand at a frequency of 2–3 Hz for 10 s. The volume of the emulsions formed was 2 mL. The evolution of the emulsions with time was observed from the side with a drop-shape analysis system (DSA 10, Krüss) at low magnification. The structure of stable emulsions over a long time was observed in situ (without dilution) with a horizontal Optiphot 2 microscope (Nikon) supplied with extra-long working-distance objectives.[12,13]

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[1] W. Ramsden, *Proc. R. Soc. London* **1903**, 72, 156 – 164.
[2] S. U. Pickering, *J. Chem. Soc.* **1907**, *91*, 2001 – 2021.
[3] B. P. Binks, *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 21 – 41.
[4] E. Vignati, R. Piazza, T. P. Lockhart, *Langmuir* **2003**, *19*, 6650 – 6656.
[5] S. Stiller, H. Gers-Barlag, M. Lergenmueller, F. Pflücker, J. Schulz, K. P. Wittern, R. Daniels, *Colloids Surf. A* **2004**, *232*, 261 – 267.
[6] B. P. Binks, T. S. Horozov, *Angew. Chem.* **2005**, *117*, 3788 – 3791; *Angew. Chem. Int. Ed.* **2005**, *44*, 3722 – 3725.
[7] D. E. Tambe, M. M. Sharma, *Adv. Colloid Interface Sci.* **1994**, 52, 1 – 63.
[8] B. R. Midmore, *Colloids Surf. A* **1998**, *132*, 257 – 265.
[9] B. P. Binks, M. Kirkland, *Phys. Chem. Chem. Phys.* **2002**, *4*, 3727 – 3733.
[10] N. P. Ashby, B. P. Binks, V. N. Paunov, *Chem. Commun.* **2004**, 436 – 437.
[11] E. J. Stancik, M. Kouhkan, G. G. Fuller, *Langmuir* **2004**, *20*, 90 – 94.
[12] T. S. Horozov, R. Aveyard, J. H. Clint, B. Neumann, *Langmuir* **2005**, *21*, 2330 – 2341.
[13] T. S. Horozov, R. Aveyard, B. P. Binks, J. H. Clint, *Langmuir* **2005**, *21*, 7405 – 7412.
[14] S. Arditty, C. P. Whitby, B. P. Binks, V. Schmitt, F. Leal-Calderon, *Eur. Phys. J. E* **2003**, 11, 273 – 281.
[15] N. D. Denkov, I. B. Ivanov, P. A. Kralchevsky, D. T. Wasan, *J. Colloid Interface Sci.* **1992**, *150*, 589 – 593.