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Inversion of Emulsions Stabilized Solely by Ionizable Nanoparticles**

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Emulsions occur as end products in a wide range of areas including the pharmaceutical, food, and cosmetic industries. They are mixtures of immiscible liquids where one liquid is dispersed as micrometer-sized drops in the continuous phase of the other.[1] To prevent separation, surfactants are usually added whose molecules cover the liquid–liquid interfaces. Recently,[2–5] it has been shown that certain solid nanoparticles act as excellent emulsifiers alone and, since particles are more strongly attached to interfaces, coalescence is absent. However, different types of particles are needed to prepare either oil-in-water (o/w) or water-in-oil (w/o) emulsions in mixtures containing equal volumes of the two liquids.[3,5–8] Herein we describe a new class of solid particle emulsifier capable of stabilizing both emulsion types efficiently. The spherical nanoparticles are those of polystyrene whose surfaces are coated with ionizable carboxylic acid groups. Inversion of the emulsion type is simply effected by either a change in the pH value or salt concentration. It should be possible to prepare a new range of stable simple and multiple emulsions by tuning the type and charge of such responsive emulsifiers.

Certain small solid particles act in many ways like surfactant molecules that adsorb at fluid–fluid interfaces and stabilize drops in emulsions and bubbles in foams.[3] It is only recently, however, that their precise role has been elucidated in surfactant-free systems. Particles stabilize emulsions in two ways:[2] In the first, they adsorb at the oil–water interface and remain there forming a film around dispersed drops and impede coalescence, and in the second, additional stabilization arises when the particle–particle interactions are such that a three-dimensional network of particles develops in the continuous phase. The enhanced

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viscosity reduces the extent of gravity-induced separation. Hydrophilic particles, for example, metal oxides, tend to stabilize o/w emulsions whereas hydrophobic particles, for example, carbon, tend to stabilize w/o emulsions.[6–8] The different tendency is linked to the contact angle θ (measured through water) that particles exhibit at the interface. Inversion of emulsions from w/o to o/w is predicted to occur as the value of θ falls below 90°. If the particles are small enough (less than a few μm), the energy ΔG required to remove a spherical particle of radius r from an oil–water interface of tension γ_{ow} is given by Equation (1).[8,9]

$$\Delta G = \pi r^2 \gamma_{ow} (1 \pm \cos\theta)^2 \qquad (1)$$

The sign inside the bracket is negative for removal into water and positive for removal into oil. When $r = 10^{-7}$ m (the size of the particles used here) and $\gamma_{ow} = 0.0533\,\mathrm{N\,m^{-1}}$ (hexadecane–water, 298 K), Equation (1) shows that the particle is most strongly held in the interface for $\theta = 90°$, with ΔG being $4.07 \times 10^5\,k_BT$. One consequence of this very high energy for the attachment of particles to fluid interfaces is that they can be thought of as irreversibly adsorbed, which is in marked contrast to surfactant molecules which adsorb and desorb. The absence of coalescence and the large range of particle types and shapes makes particle-stabilized emulsions attractive.

Control of the type of emulsion is important, as is the ability to invert from one to the other. Until now, obtaining both types of emulsion in a particular oil–water system was only possible by utilizing particles of different wettability,[5,8] by changing the oil:water ratio,[10] or by adding surfactant which adsorbs on particle surfaces and modifies their wettability in situ.[2] These routes may not be suitable in many cases. We describe here a simple strategy to invert these emulsions by using polystyrene nanoparticles whose surfaces contain carboxylic acid groups. Particles can be made sufficiently more or less hydrophilic for them to stabilize both types of emulsion in the same system by controlling the degree of charge on the particle surfaces (by changing the pH value or addition of salt). It was not possible to achieve this degree of control previously. Polystyrene particles containing surface sulfate groups preferentially formed w/o emulsions,[11] that is, these particles are relatively hydrophobic. In contrast, polystyrene particles with grafted copolymer molecules containing amine groups stabilized only o/w emulsions[12] since the particles were rendered more hydrophilic.

Spherical, monodisperse, surfactant-free polystyrene particles can be synthesized with different densities of carboxylic acid groups on their surfaces. Under conditions where these groups are predominantly un-ionized (COOH), the particles are expected to be more hydrophobic and stabilize water drops in oil relative to ionizing conditions (COO$^-$) in which the particles are more hydrophilic and should stabilize oil drops in water. Hexadecane–water emulsions (1:1 by volume) with particles of 200-nm diameter and high surface charge density (101 $\mu\mathrm{C\,cm^{-2}}$) were o/w at all pH values between 2 and 11 and salt (NaCl) concentrations between 0 and 2 M. The same sized particles act as excellent emulsifiers for both emulsion types, however, when the charge density is reduced (12.7 $\mu\mathrm{C\,cm^{-2}}$). Figure 1 shows the variation of the emulsion conductivity (immediately after preparation) with the pH value of the aqueous phase in systems containing 1 M NaCl. Up to pH 9.5, emulsions are of low conductivity (similar to pure oil), disperse in oil and not water, and are therefore w/o. Inversion (dotted line) to highly conducting (similar to aqueous NaCl) o/w emulsions, which disperse in water and not oil, occurs just below pH 10.0. The inset illustrates the effect of the pH value on the position of these particles at an interface. We note that emulsions were w/o at all pH values in the presence of 0.01 M NaCl and could not be inverted in this way.

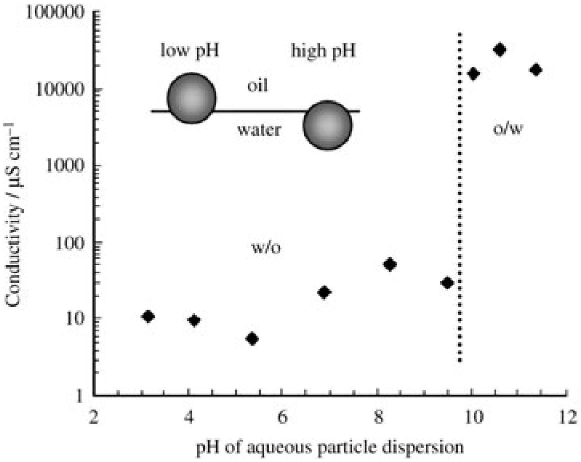

Figure 1. Inversion of particle-stabilized emulsions by changing the pH value. The plot shows the conductivity of emulsions of hexadecane and 1 M aqueous NaCl (1:1) stabilized by 2 wt% of carboxy-coated polystyrene latex particles (200 nm diameter) at different pH values. Emulsions are w/o below pH 9.5 and o/w at pH ≥ 10.0. The inset depicts the change in the position of a particle at the interface; low pH: $\theta > 90°$ and high pH: $\theta < 90°$.

The appearance of the emulsions at high salt concentration is shown in Figure 2 for different pH values, one year after preparation. All emulsions were completely stable to coalescence, as shown by no visible separation of the dispersed phase occurring and the drop-size distributions determined by light diffraction studies remaining unchanged. Since the density of hexadecane is less than that of water, sedimentation of the w/o emulsions occurs over time, with a clear oil phase separating above (3 vials on left), whereas o/w emulsions cream to the top of the vessel as a clear water phase drains below (3 vials on right). Although the dispersed phase volume fraction in both the sedimented and creamed emulsions increases from 0.5 to over 0.75, the emulsion drops remain stable to coalescence because the adsorbed layers of polystyrene particles act as a mechanical barrier to fusion. To visualize the particles around drops emulsions were prepared at low and high pH values using larger particles (3.2 μm diameter) of approximately the same surface charge density (11.8 $\mu\mathrm{C\,cm^{-2}}$). Optical micrographs of similar-sized emulsion drops are shown in Figure 3. The left image is that of a water drop in oil formed at a low pH value. The particles

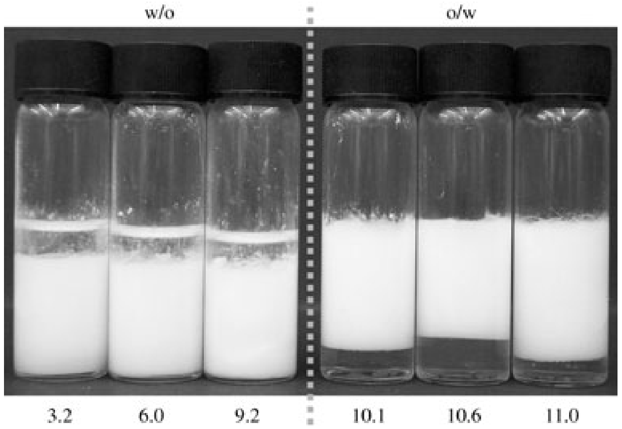

Figure 2. Appearance of vials at 25 °C of systems containing hexadecane and 1 M aqueous NaCl (1:1) and 2 wt% carboxy-coated polystyrene latex particles of 200 nm diameter as a function of the pH value (given). Emulsions (white) are w/o at pH $\leq$ 9.5 (left) and undergo sedimentation to liberate a clear oil phase above, and are o/w at pH $\geq$ 10.0 (right) which cream with a clear aqueous phase separating below. All emulsions are completely stable to coalescence.

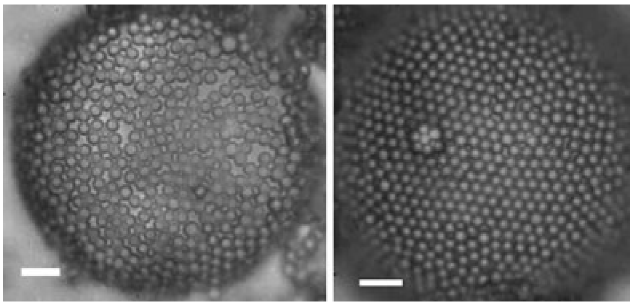

Figure 3. Optical micrographs of single w/o (left) and o/w (right) emulsion drops in hexadecane:1 M aqueous NaCl mixtures (1:1) stabilized by 3.2-μm diameter carboxy-coated polystyrene latex particles. The water drops are favored at low pH values (< 9.5) and particles are less than close-packed at their interfaces. The oil drops are favored at high pH values ($\geq$ 10.0) and particles are hexagonally close-packed. Scale bars are 10 μm.

cover most of the oil–water interface, but arrange themselves in a liquidlike order with parts of the interface devoid of particles. We observed that particles in the aqueous dispersions before emulsification were strongly flocculated at low pH values because of the absence of repulsion between uncharged COOH groups on the surface. It appears that some of the flocs adsorb intact to interfaces of the drop leaving voids between them. In contrast, the image on the right is that of an oil drop in water formed at a high pH value in which particles appear hexagonally close-packed over the entire interface. Dissociation of the acid groups occurs at these high pH values, and repulsion between like-charged particle surfaces in the bulk phase causes breakup of the flocs and results in a dispersion of discrete particles to be stabilized.

It is difficult to test our hypothesis that raising the pH value results in hydrophobic particles becoming increasingly hydrophilic, since a reliable method for determining the contact angles of submicron-sized particles at oil–water interfaces does not exist. However, the idea is given some credence from the contact angle data of water drops under oil on monolayers of a long-chain carboxylic acid adsorbed through a terminal thiol group on to gold.[13] The value of θ (through water) for a dilute layer of surface COOH groups decreases from 104° at pH 2 through 90° to 67° at pH 13 as the acid groups ionize and become more wettable by water. This decrease is in line with emulsion inversion from w/o to o/w with increasing pH value.

Charged particles are also sensitive to the presence of electrolyte.[14,15] A second way to effect emulsion inversion is to start with a hydrophilic system that forms an o/w emulsion and reduce the salt concentration, thus rendering the system more hydrophobic. Table 1 summarizes the influence of NaCl concentration on the conductivity and type of 1:1 emulsions stabilized by the same particles above: at high pH value, they invert from o/w to w/o on lowering the salt concentration to 0.6 M, as predicted. All emulsions were stable to coalescence. In summary, emulsions stabilized by ionizable carboxy-coated polystyrene nanoparticles invert from w/o to o/w upon increasing either the pH value or salt concentration as the particles become more hydrophilic. The reason for this change is that the degree of ionization of the surface acid groups increases not only with pH value but also with salt concentration.[14–16] A relatively high pH value (10) is required for inversion compared with the pH value for 50% ionization (pK_a) of a short-chain carboxylic acid in bulk water (4.8). Acid dissociation is more energetically unfavorable when such groups are at an interface (particle or drop) compared with isolated groups in the bulk phase because of the proximity of other similarly charged groups, which generate a surface potential ψ. For the particles used here, the area per charged group is approximately 1.25 nm^2. Protons are held more strongly at the surface and the surface pH value is lower than that in the bulk phase because of the existence of an electrostatic field around a negatively charged particle. Dissociation of weak acid groups on a surface will therefore only be complete at higher pH values in solution relative to that of a weak acid in the bulk phase. The addition of salt causes a reduction in the value of ψ and promotes further dissociation.

Table 1: Effect of salt concentration on the conductivity (κ) and type of emulsions prepared.[a]

NaCl [M]	κ [μS cm^{-1}]	Type
0.30	20.5	w/o
0.42	26.8	w/o
0.47	33.4	w/o
0.54	34.2	w/o
0.66	17720	o/w
0.79	21200	o/w
1.15	31500	o/w
2.15	49500	o/w

[a] From hexadecane and aqueous NaCl (1:1) containing 2 wt% of carboxy-coated polystyrene latex particles (200 nm diameter) at pH 10.6 at 25 °C.

Nanoparticles are effective emulsifiers of oil and water and, by controlling the extent of charge on their surfaces, ultrastable emulsions of both o/w and w/o can be prepared. Emulsion inversion is simply achieved by changing the pH value or salt concentration if the surface groups are ionizable. Manipulating the behavior of particles adsorbed at fluid interfaces in this way enables the development of a novel range of simple and multiple emulsions for use in food, drug, and cosmetic formulations.

Experimental Section

Methods: The pH value of aqueous dispersions of carboxy-coated, spherical, monodisperse polystyrene latex particles (IDC, Oregon) was adjusted with HCl or NaOH after addition of NaCl electrolyte. Batch emulsions of equal volumes of hexadecane and an aqueous dispersion of the particles were prepared by using an Ultra Turrax T25 homogenizer (1 cm head) operating at 11000 rpm for 2 min. Their type was determined by measuring the conductivity and by the drop test. Their stabilities at 25 °C were measured by monitoring the movement of the oil–emulsion and water–emulsion interfaces. Drop-size distributions were measured by using a Malvern MasterSizer 2000 instrument. For microscopy studies, a dilute sample of emulsion was placed in a haemocytometer cell (Weber Scientific) and viewed with a Nikon Labophot microscope fitted with a DIC-U camera (World Precision Instruments). Images were processed by using Adobe Photoshop 5.0 software.

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