Nanoparticles

Temperature-Induced Inversion of Nanoparticle-Stabilized Emulsions**

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Emulsions are mixtures of immiscible liquids where one liquid is dispersed as micrometer-sized drops in the continuous phase of the other. They occur as end products in a wide range of areas including the food, cosmetic, and pharmaceutical industries. To prevent phase separation, surfactants or proteins are usually added to cover the liquid–liquid interfaces.[1] It has been shown recently that certain solid nanoparticles act as excellent emulsifiers alone[2–5] and novel materials can be made from them.[6,7] Inversion of such emulsions from oil-in-water (o/w) to water-in-oil (w/o) or vice versa can be effected by changes in the oil:water ratio,[8] pH value,[9] or oil type.[10] Herein we describe for the first time temperature-modulated emulsion inversion using sterically stabilized polystyrene latex particles as the sole emulsifier. The steric stabilizer is a diblock copolymer in which one block is thermo-responsive, exhibiting inverse temperature solubility behavior. Thus the particle surface becomes less hydrophilic at higher temperature, causing inversion from o/w to w/o to occur in batch emulsions.

Emulsions stabilized by ionic surfactant invert from w/o to o/w with increasing temperature as a result of the increased dissociation of counterions bound to surfactant head groups, making the surfactant more hydrophilic.[11] In contrast, nonionic surfactant-stabilized emulsions invert the other way around; increasing temperature causes dehydration of head groups, making them more hydrophobic.[11] Inversion with respect to temperature is important industrially and is exploited to prepare fine emulsions of increased stability.[12] Small solid particles act in many ways like surfactant molecules in that they adsorb at fluid–fluid interfaces, allowing stabilization of droplets in emulsions and bubbles in foams.[3] However, it is only recently that their precise role has begun to be elucidated in surfactant-free systems. The wettability of the particles at the oil–water interface is crucial in determining which type of emulsion is formed, with hydrophilic particles preferentially forming o/w emulsions and hydrophobic particles forming w/o emulsions. Although the influence of temperature on the stability of either w/o[13] or o/w[14] emulsions stabilized solely by nanoparticles has been reported, the ability to phase invert such emulsions with temperature has not been demonstrated.

The particulate emulsifier employed in this study was a sterically stabilized polystyrene (PS) latex of 152 nm diameter. The steric stabilizer was a near-monodisperse diblock copolymer, poly[2-(dimethylamino)ethyl methacrylate-*block*-methyl methacrylate], PDMA-*b*-PMMA.[15] The hydrophobic PMMA block is designed to adsorb onto the latex surface and the solvated PDMA block acts as the hydrophilic steric stabilizer. As reported earlier,[16] the cationic charge density of the PDMA block can be adjusted by controlling the solution pH value and this dictates the emulsification performance of these PS latex particles. At 25 °C, batch emulsions containing equal volumes of *n*-hexadecane and 2 wt% aqueous PS latex are o/w at all pH values above 3, and the stability of these emulsions towards coalescence increases progressively on increasing the pH from 3 to 8. It was argued that this effect was due to progressive deprotonation of the PDMA-based stabilizer chains with increasing pH, causing the sterically stabilized PS latex particles to become less hydrophilic and hence better emulsifiers.[16]

In this work, we investigate the effect of temperature on emulsions stabilized by the same particles as above, prepared at pH 8.1, which are completely stable to coalescence at 25 °C. In one series of experiments, an *n*-hexadecane/water (1:1) emulsion stabilized by 2 wt% particles was prepared at room temperature and heated progressively up to 70 °C with gentle shaking. Although the emulsion remained o/w at all temperatures, substantial coalescence occurred at and above 60 °C. In a second series, an emulsion was prepared at each temperature after pre-equilibration of the two phases at that temperature. The difference between the two is that particles are already adsorbed at oil–water interfaces in the first series, whereas they are free to become adsorbed at different temperatures in the second series. Importantly in the second series, phase inversion of the emulsions occurs from o/w at low temperatures to w/o at higher temperatures. This result is shown in Figure 1, which summarizes the emulsion conductivities (κ) and the drop test findings obtained at various temperatures. At temperatures below 52 °C, the conductivities are relatively high ($\kappa_{aq} = 25$, $\kappa_{oil} = 0.1\ \mu S\,cm^{-1}$), the emulsions disperse in water and not in oil and are therefore water continuous. At and above 65 °C, the emulsions exhibit low conductivities, disperse in oil rather than in water, and are therefore oil continuous. At intermediate temperatures indicated by the dotted lines (53–64 °C), emulsions can be either of the two types, which may co-exist.

Optical micrographs of the emulsions of the second series are shown in Figure 2. At 25 °C (Figure 2 a) oil drops in an o/w emulsion are discrete and some appear non-spherical. At 55 °C (Figure 2 b) in addition to simple emulsions, there is some evidence for multiple emulsions, in this case of water-in-oil-in-water (w/o/w), in which water drops are present within oil globules themselves dispersed in water. The appearance of

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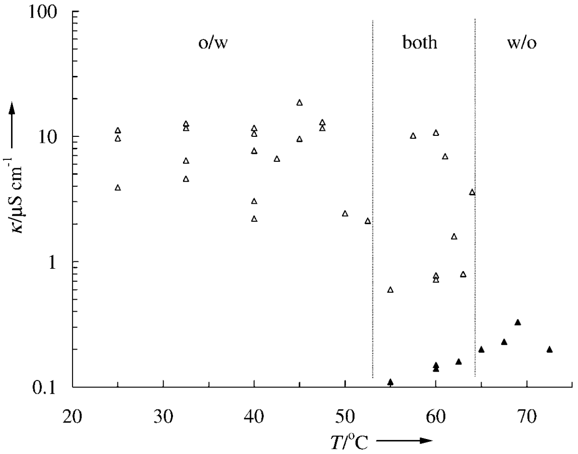

Figure 1. Conductivity κ of batch emulsions (second series, see text for details) comprising equal volumes of *n*-hexadecane and 2 wt% aqueous PDMA-*b*-PMMA-stabilized PS latex (152 nm diameter, pH 8.1) as a function of temperature. Emulsions are only o/w (△) to the left of the first dotted line and only w/o (▲) to the right of the second dotted line, but can be either type or multiple at intermediate temperatures. The labels for emulsion type are based on drop test results.

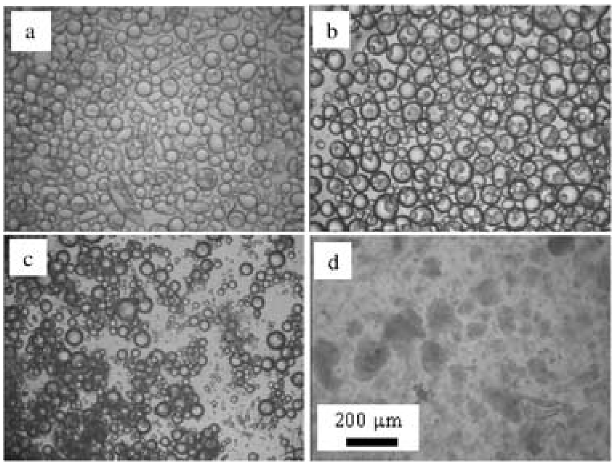

Figure 2. Optical micrographs of emulsions prepared as in Figure 1 at a) 25 (o/w), b) 55 (w/o/w), and c) 65 °C (w/o). Also shown is micrograph of the 2 wt% aqueous PS latex (pH 8.1) held at 70 °C for 30 min on a glass slide (d). The scale bar refers to all images.

multiple emulsions around conditions of phase inversion in surfactant-stabilized systems is common; the balanced surfactant satisfies the preference for both types of emulsion simultaneously.[12] Such emulsions are notoriously unstable to coalescence (of both drops and globules), whereas these solid-particle-stabilized emulsions are stable. The stabilization of multiple emulsions by only one type of particle has been reported for silica.[17] At 65 °C, water drops in a w/o emulsion are characteristically flocculated (Figure 2c), since any repulsion between particle surfaces on neighboring drops is mediated through the oil phase, which has a low dielectric constant, and little steric stabilization is provided by the PDMA chains in this oil.

A measure of the average diameter of drops in both types of emulsion is plotted against temperature in Figure 3. For o/w emulsions, the number-average mean determined by optical microscopy (40 drops) is shown, as is the median diameter measured using light diffraction. For w/o emulsions, only the mean by microscopy has been determined. The average oil-drop size increases with temperature on approaching inversion and the size of water drops is less than that of oil drops. Assuming that particles form a hexagonally close-packed monolayer around oil drops, we calculate that at 25 °C approximately 35% of the particles originally in water become adsorbed around drops of average diameter 76 μm. This number falls to 24% for the larger drops of 113 μm at 50 °C. On this basis, there is thus a distribution of particles between interface and bulk, although no exchange is likely because of the high energies of particle attachment to interfaces.[3]

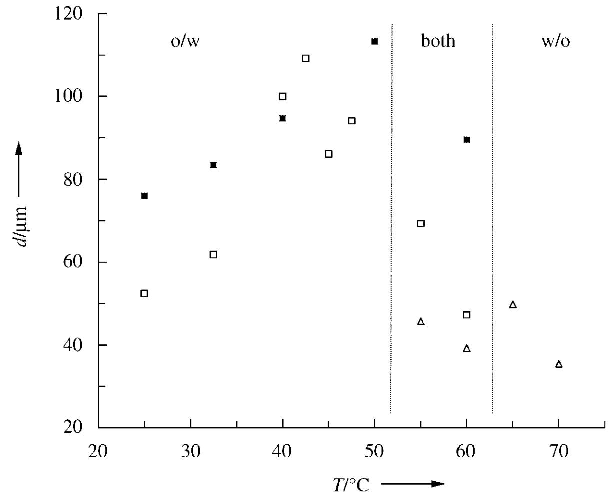

Figure 3. Average drop diameter *d* versus temperature for batch emulsions prepared as in Figure 1 immediately after preparation. Sizes determined by optical microscopy (□ o/w, △ w/o) and using light diffraction (■ o/w) are shown.

The stabilities of these latex-stabilized emulsions six months after preparation are summarized in Figure 4. The parameters *f*(oil) (and *f*(water)) are defined as the volumes of oil (or water) resolved relative to the initial volumes of oil (or water). At temperatures prior to inversion, the oil drops in o/w emulsions cream within 1–2 h at all temperatures with no further change subsequently. The oil volume fraction in the cream is now increased beyond 0.5 and, apart from the stable emulsion at 25 °C, a low degree of coalescence occurs in emulsions approaching 50 °C. At intermediate temperatures (between the dotted lines), the creaming of o/w emulsions is reduced and w/o emulsions sediment but are stable to coalescence. At temperatures above inversion, sedimentation of water drops occurs gradually in the first 24 h followed by their coalescence. Eventually, virtually complete phase separation ensues as indicated by near unity values of both *f*(oil) and *f*(water).

We seek to understand the origin of emulsion phase inversion with temperature, which occurs in the same sense as that for non-ionic surfactants. Some clues to this can be found in the behavior of the aqueous PS latex particle dispersions in the absence of oil. Dynamic light-scattering studies indicate

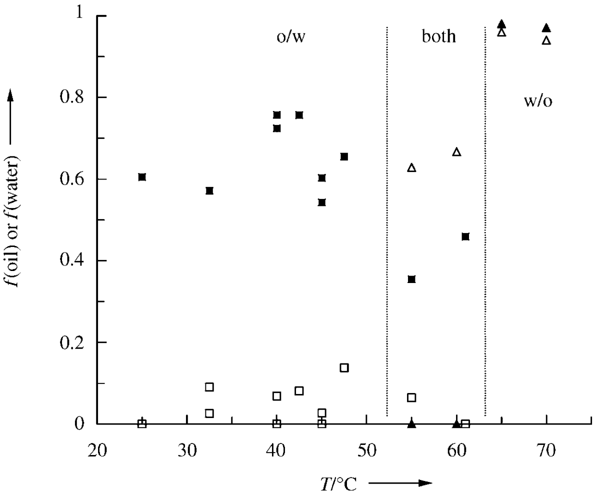

Figure 4. Stability of batch emulsions after six months at different temperatures. For o/w, *f*(water) (■) relates to creaming and *f*(oil) (□) relates to coalescence. For w/o, *f*(oil) (△) relates to sedimentation and *f*(water) (▲) relates to coalescence.

that the mean hydrodynamic diameter remains constant at 152 nm between 20 and 50 °C and increases to 173 nm at 53 °C, above which significant flocculation is apparent. Optical microscopy investigations of a drop of dispersion on a glass slide shows no features above 1 μm up to 50 °C but particle aggregates of increasing size above this critical temperature (Figure 2 d). Since PDMA homopolymer in water at pH 8.1 exhibits a lower consolute solution temperature between 32 and 46 °C (depending on its mean degree of polymerization),[18] it is likely that the temperature-induced flocculation of the latex particles reflects the thermo-responsive character of the PDMA block in the stabilizer chains. This hypothesis was verified by performing contact-angle measurements of water drops under *n*-hexadecane on spin-coated films of PDMA homopolymer at different temperatures. As shown in Table 1, the contact-angle measured through water increases with temperature from near-wetting (hydrophilic) at 25 °C to values that are characteristic of hydrophobic surfaces above 60 °C. They are also in line with the predicted change in the wettability of the particles in emulsions, from predominantly hydrophilic at low temperatures (o/w) to more hydrophobic at high temperatures (w/o).

Table 1: Effect of temperature on the contact angle θ of a water drop.[a]

T [°C]	θ (w/o) [°]	θ (o/w) [°]
25	4	3
35	6	6
45	11	12
55	28	28
60	34	32
65	33	30
75	58 ± 10	65 ± 10

[a] At pH 8.1 under *n*-hexadecane, measured through water, on a glass slide coated with a film of PDMA homopolymer. Data given for water (w/o) or oil (o/w) contacting the substrate first.

Two competing effects caused by increasing temperature may cause this change. The first is the disruption of hydrogen bonds surrounding the PDMA chains, leading to an increase in their hydrophobicity. The second is an increase in the degree of protonation of tertiary amine groups resulting in increased particle hydrophilicity. For trimethylamine in water, this has been measured as an increase in K_b (equilibrium constant) with temperature, taking into account the increase in the dissociation constant of pure water.[19] It is therefore clear that for these sterically stabilized PS latex particles, the dominant influence of temperature is in reducing the degree of hydration of the PDMA chains to such an extent that these particles become preferentially wetted by oil.

Nanoparticles are effective emulsifiers of oil and water. Appropriate design of the latex surface allows the particle wettability to be controlled by adjusting the temperature, which in turn allows the preparation of either o/w or w/o emulsions. The emulsions described herein are temperature-dependent but not temperature-responsive. Manipulating the behavior of particles adsorbed at fluid interfaces in this way augurs well for the development of a novel range of simple and multiple emulsions for use in cosmetic, food, and drug and formulations.

Experimental Section

The synthesis and characterization of the PDMA-*b*-PMMA-stabilized PS particles (diameter = 152 nm, $M_n = 38\,400\ \mathrm{g\,mol^{-1}}$, $M_w/M_n = 1.14$) was described earlier.[15,16b] Dynamic light scattering of 2 wt % aqueous PS latex at pH 8.1 was measured using a Malvern Nano ZS ZEN3600 instrument under a N_2 atmosphere at a scattering angle of 173°. Three measurements were made at each temperature, with 30 min being allowed for equilibration. Batch emulsions of equal volumes (2 mL) of *n*-hexadecane and aqueous PS latex (pH 8.1), equilibrated at the appropriate temperature, were prepared at that temperature using an Ultra Turrax T25 homogenizer (1 cm head) operating at 11 000 rpm for 2 min. Emulsion type was determined by conductivity measurements and the drop test. Their stabilities at different temperatures were measured by monitoring the movement of the oil–emulsion and water–emulsion interfaces. Drop size distributions of o/w emulsions were measured using a Malvern MasterSizer 2000 instrument using either cold or hot water as diluting phase. For microscopy, a dilute sample of emulsion/dispersion 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 using Adobe Photoshop 5.0 software. The contact angles of water drops (10 μL, pH 8.1) under *n*-hexadecane on films of PDMA homopolymer ($M_n = 21\,300\ \mathrm{g\,mol^{-1}}$) spin-coated onto glass slides from a 5 wt % solution in methanol (Speciality Coating Systems model P6700, 2000 rpm for 1 min) were determined using a Krüss DSA10 apparatus with a thermostatted cell. At least five separate drops were used at each temperature.

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