



Inversion of particle-stabilized emulsions of partially miscible liquids by mild drying of modified silica particles

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ARTICLE INFO

Article history:

Received 31 January 2011

Accepted 22 March 2011

Available online 27 March 2011

Keywords:

Pickering emulsion
Transitional inversion
Bijel
Binary fluid
Drying
Hydration
Adsorption
Stöber silica
Colloidal particles
2,6-Dimethylpyridine

ABSTRACT

Using a system of modified silica particles and mixtures of water and 2,6-lutidine to form particle-stabilized emulsions, we show that subtle alterations to the hydration of the particle surface can cause major shifts in emulsion structure. We use fluorescence confocal microscopy, solid state nuclear magnetic resonance (NMR) and thermo-gravimetric analysis (TGA) to explore this sensitivity, along with other shifts caused by modifications to the silica surface chemistry. The silica particles are prepared by a variant of the Stöber procedure and are modified by the inclusion of 3-(aminopropyl)triethoxysilane and the dye fluorescein isothiocyanate. Treatment prior to emulsification consists of gently drying the particles under carefully controlled conditions. In mixtures of water and 2,6-lutidine of critical composition, the particles stabilize droplet emulsions and bijels. Decreasing particle hydration yields an inversion of the emulsions from lutidine-in-water (L/W) to water-in-lutidine (W/L), with bijels forming around inversion. So dependent is the emulsion behavior on particle hydration that microscopic differences in drying within a particle sample can cause differences in the wetting behavior of that sample, which helps to stabilize multiple emulsions. The formation of bijels at emulsion inversion is also crucially dependent on the surface modification of the silica.

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1. Introduction¹

Recently we [1–3] and others [4–7] have harnessed liquid–liquid demixing to create convoluted interfaces on which to organize colloidal particles. Our approach has been to disperse the particles in the single fluid phase at the critical composition and then to change the temperature such that the liquids phase-separate via spinodal decomposition. Appropriately tailored particles become trapped at the liquid–liquid interface and this leads to the formation of a bicontinuous, interfacially jammed emulsion gel (bijel) [8]. By varying the liquid composition, demixing via nucleation and growth can be used to create particle-stabilized droplet

emulsions [2,9]. Further, with subtle variations in particle treatment we have demonstrated that it is possible to create particle layers that retain stability once the liquid–liquid interface has been removed [10]. While exploring these approaches we have tacitly assumed that the particle surfaces can be simply characterized by a three-phase contact angle and that the liquid–liquid phase diagram is unperturbed by the presence of the particles. Of course, both are over-simplifications.

Bijel formation relies on careful tuning of particle surface chemistry to give a three-phase contact angle close to 90° and builds on previous work on transitional emulsion inversion [11]. Particle-stabilized emulsions will invert from oil-in-water (O/W) to water-in-oil (W/O) if the initially hydrophilic particle surfaces are made progressively more hydrophobic. In practice this has usually been achieved with fumed silica particles by methylating a proportion of the surface silanol (SiOH) groups. A standard route is to vary the concentration of the silanizing agent (dichlorodimethylsilane) to change the degree to which the silica surfaces become hydrophobic [12]. Alternatively, polystyrene particles can be used to induce transitional inversion in an analogous manner. Read et al. showed that, by using block co-polymers to provide a steric barrier on polystyrene particle surfaces, emulsions of intermediate polarity oils can be made that will undergo transitional inversion

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¹ The following abbreviations are used in this report. Following the convention of oil–water emulsions, a lutidine-in-water emulsion is designated L/W, water-in-lutidine W/L, and a water-in-lutidine-in-water multiple emulsion W/L/W. For conciseness, the lutidine-rich phase and water-rich phases that comprise the binary fluid are referred to respectively as the L-phase and W-phase. Three types of silica particles are referred to: these are Fluor-S (fluorescently tagged silica), Amino-S (silica modified with amino groups) and Plain-S (unmodified silica). The preparation of these particles is described in Section 2.

in response to a change in pH [13]. Here the cationic charge density of the outer polymer block is controlled by the pH and this modifies the wettability. One of us used the same particles to demonstrate transitional inversion induced by a change in temperature [14]. Phase inversion occurred on warming from 25 °C to 60 °C provided that a new emulsion was made at each temperature. A reduction in the degree of hydration of the outer polymer block gave rise to hydrophobic particle surfaces at elevated temperatures. In this work we explore particle pre-treatment and surface chemistry and the influence these have on transitional emulsion inversion using monodisperse silica particles.

The binary liquid system used here is 2,6-lutidine (2,6-dimethylpyridine) and water, which has a lower critical solution temperature (LCST) at atmospheric pressure of 34.1 °C and a critical lutidine mole fraction of $x_l = 0.064$ [15]. In our experiments we induce phase separation by heating the lutidine–water mixture (pressure quench is a viable alternative [16]). The interfacial tension grows from zero on heating through the critical point and by 40 °C has reached 0.22 mN/m [17]. At this temperature the water-rich phase occupies 61.1% of the volume and has density of 0.992 g/cm³; the lutidine-rich phase occupies the remaining 38.9% and has a similar density (0.958 g/cm³).

We employ silica colloidal particles synthesized using the Stöber procedure [18] or modifications to it. Drying the particles affects both their surface chemistry (as synthesized, Stöber silica has a surface coating of silanol groups) and the quantity of physically bound water. We use this effect to tune the wettability of the particles. There is disagreement in the literature about the onset temperatures of the various phenomena; we will refer to Iler [19] and to Zhuravlev [20] as representative bodies of work. The first three stages of Zhuravlev's model are pertinent here. In stage 1 (25 °C), the silica surface is hydroxylated and is covered with a complete layer of physically adsorbed water. In stage 2 (25–190 °C), the silica surface continues to be in a state of maximum hydroxylation; it is covered by one layer or a partial layer of water which is completely removed by the time the upper temperature of the range has been reached. During stage 3 (190–400 °C), the degree of hydroxylation of the silica surface decreases significantly; siloxane bridges form via a condensation reaction. For Iler the boundary between stage 2 and stage 3 is at a slightly lower temperature. He reports that silanol groups will begin to condense and evolve water extensively above about 170 °C, with half of the hydroxyl groups having been removed by 400 °C. Further to this, the activation energy for hydroxylation and dehydroxylation will also be modified by the presence of different chemical groups on the particle surfaces.

The adsorption of molecules onto the surface of silica has been extensively studied [21]. Here we are interested in the small organic molecule 2,6-dimethylpyridine which is quite similar to 2,5-dimethylpyridine and 2,4,6-trimethylpyridine which were studied by Privat et al. [22,23]. The fumed silica used in those experiments had <3 OH nm⁻² compared to the 4.6 OH nm⁻² typical for solution-prepared silica [20]. The remaining surface may well be occupied by siloxane bridges. Using NMR they ruled out interaction between the nitrogen lone pair and the silanol groups [23]; instead they concluded that the molecules form a π -bond with the oxygen of surface siloxane groups or with deprotonated silanol groups (hence the molecules lie flat on the surface). The adsorption isotherms for these molecules have a step-like shape indicative of the formation of successive layers presumably by π -stacking. It is important to note that pyridine rings with multiple methyl side groups appear to behave very differently to pyridine rings alone (and also 4-picoline [24]). In the latter cases, adsorption occurs via bonding between the nitrogen lone pair and the surface silanol group and the molecule orients perpendicular to the surface [21].

The wetting character of silica surfaces in water–lutidine mixtures is complex. Prior to demixing, lutidine preferentially adsorbs onto the silica surfaces [25]. This occurs at the critical composition but is more pronounced as the lutidine concentration is reduced. Between the phase separation temperature and the wetting transition temperature there is a range over which the one phase completely wets the silica surface. For flat silica surfaces the wetting transition temperature can be as much as 15 °C above the LCST [26] but changes depending on the pre-treatment of the silica surfaces. Although pre-washing a flat surface with lutidine suppresses the transition temperature [27], for all observations we are aware of it is the water-rich phase that wets the surface. The situation with particles may be different. For polystyrene spheres the wetting transition temperature falls to a fraction of a degree above the LCST; however, particles with different surface chemistries are wet by different phases [28]. At higher temperatures, for flat plates and particles, silica exhibits partial wettability with both water-rich and lutidine-rich phases [26]. Hence a warming route that starts in the single fluid phase and goes through and beyond the critical point will encounter sequentially: lutidine adsorption, wetting by the water-rich phase and finally partial wettability.

The inversion of particle-stabilized emulsions has previously been implemented by adsorption to the particle surfaces. Specifically, a double-chained cationic surfactant was used to systematically modify the wettability of silica particle surfaces [29]. At low surfactant concentration the positively charged surfactant is adsorbed onto the negatively charged silica; the chains protrude making the surfaces partially hydrophobic. As the concentration is increased the coated particles become effective for stabilizing water droplets in oil (the original particles stabilize oil droplets in water). At very high surfactant concentrations the situation is reversed and any similarity to the silica/lutidine behavior ceases. The particle surfaces become hydrophilic again which may well be a consequence of a surfactant bilayer forming around the particles. The exposed surfactant head group renders the surface positively charged, leading to a second transitional inversion to oil droplets in water. Single-chained surfactants do not make the particle surfaces hydrophobic enough to effect an inversion.

In this work we specifically study the influence of drying on the behavior of silica particles in water–lutidine mixtures. This new method of tuning emulsion structures shows an unexpectedly high degree of sensitivity, and has been crucial in understanding the formation of bijels in the water–lutidine system. During these investigations we have shown that the wetting character of silica surfaces can change during phase separation. Although the interplay between phase separation and wetting has been explored for many years, this is the first observation of its kind. Confocal microscopy is used to provide such time-resolved information while TGA is used to show the stages of particle drying and NMR is used to illustrate the change in balance between physisorbed water and H-bonded silanol groups with drying protocol. A key conclusion regards the location and orientation of lutidine molecules at the silica surface.

2. Materials and methods

2.1. Particle synthesis

The fluorescent dye is prepared [30] by reacting 0.0357 g (0.0917 mmol) of fluorescein isothiocyanate (FITC; 90%, Sigma Aldrich) with 0.1827 g (0.8252 mmol) of 3-(aminopropyl)triethoxysilane (APTES; Sigma Aldrich) and then stirring for 24 h. The resulting slurry is then dissolved in 1.3 ml of anhydrous ethanol to give a clear, orange solution which is stored in a refrigerator prior to use. The product is N-1-(3-triethoxysilylpropyl)-N'-

fluoresceyl thiourea (APTES-FITC). As it may be assumed this is a 1:1 reaction (*i.e.* one APTES molecule reacts with one FITC molecule) it should be noted that the APTES is in excess.

Silica particles are formed from the condensation of tetraethyl orthosilicate (TEOS; Sigma Aldrich, distilled before use) in ethanol with ammonia solution (NH₄OH) in water as catalyst [30,31]. Both the concentration of ammonia and water affect the final particle size.

2.1.1. Fluorescent silica particles (designated Fluor-S)

1.5 l of ethanol and 186 ml of a 35% solution of NH₃ in water were placed in a 2 l bottle. The bottle was cooled in a fridge to 10 °C for 3 h. To this was added 60 ml of distilled tetraethyl orthosilicate and three batches of APTES-FITC solution. The reagents were left in the refrigerator for 24 h and allowed to react.

2.1.2. Non-fluorescent APTES-modified silica particles (designated Amino-S)

The aim of this preparation is to make a silica dispersion the same as Fluor-S but without the fluorescein which may have surfactant properties. 375 ml of ethanol and 46.5 ml of a 35% solution of NH₃ in water were placed in a 500 ml sample bottle which was stored in a refrigerator at 10 °C for 3 h. To this were added 15 ml of TEOS and the contents of an ampoule containing 0.1370 g APTES and 0.975 ml ethanol. The reagents were left in the refrigerator for 24 h and allowed to react.

2.1.3. Fluorescent silica core/pure silica shell particles (designated Plain-S)

The aim of this preparation was to make a fluorescent silica colloid that had native silica surfaces. 1.5 l of ethanol and 186 ml of a 35% solution of NH₃ in water were placed in a 2 l bottle. The bottle was cooled in a fridge to 10 °C for 3 h. To this were added 60 ml of distilled TEOS and three batches of APTES-FITC solution. The reagents were left in the refrigerator for 24 h and allowed to react. The resulting particles were cleaned to remove excess dye and unreacted reagents by being spun in a centrifuge and then re-dispersed in an ethanol solution containing 10% NH₃. After the twentieth wash the particles were spun and re-dispersed in an ethanol solution containing 0.25% NH₃ which resulted in a suspension with a mass fraction of 0.095. 20 ml of this was taken and diluted to 600 ml using the ethanol solution containing 0.25% NH₃ and to this was added 10 ml of TEOS. The reagents were allowed 24 h to react. No small silica particles were subsequently found in the dispersion so it is assumed that all the TEOS formed a shell around the fluorescent silica core particles (as opposed to nucleating new spheres).

In summary we have prepared the following particles (sized using dynamic light scattering):

Fluor-S, radius 380 nm (homogeneous-fluorescent silica only; contains APTES and APTES-FITC);

Amino-S, radius 428 nm (non-fluorescent silica; contains APTES);

Plain-S, radius 345 nm (core-shell; fluorescent core, pure silica shell).

2.2. Particle treatment

The Stöber synthesis used to produce all these particles results in a suspension of particles in an ammonia/ethanol mixture. Before use, the particles undergo a washing/drying process. In all cases, the particles are washed twice with ethanol and four times with water. Each wash consists of dispersing the particles in the solvent with a sonic probe (approx. 8 W, 60 s), agitating for at least an hour, and centrifuging to separate the particles. After washing,

the particles, forming a cake approximately 1 cm deep at the bottom of a 20 ml glass vial, are placed in an oven overnight at 30 °C. The dried cake is crushed with a mortar and pestle. This is referred to as the 'initial drying'.

To prepare the particles for use in water-lutidine emulsions or bijels, further drying is generally necessary to adjust their wetting properties and make them surface-active. The particles (500 mg or as little as is required) are spread as thinly as possible in a glass Petri dish. Avoiding particle clumps or a thick layer of particles improves the evenness of the drying and hence the reproducibility of the results. The dish is placed in a pre-heated vacuum oven at the required temperature and with the vacuum on. If the drying time is half an hour or longer, the reproducibility can be improved by removing the particles every 15 min and shaking the dish to re-distribute them.

Presumably because of differences in size and porosity, different batches of the same type of particle often require varying temperatures or times to produce the same properties. Following the initial drying, a good starting point in identifying the right combination was to dry a small sample of particles for 30 min at 170 °C and test their emulsion behavior. This use of a (relatively) high temperature speeds up the process of identifying the right drying protocol. The time and/or temperature can be adjusted according to the results of the test.

To some extent, particles that are too dry can be re-hydrated (by soaking in water for several days) and then re-used. However, if the drying temperature is high (180 °C or above), re-hydration becomes harder to achieve, and may require extended boiling. At these temperatures, surface silanol groups begin to condense into siloxanes, and the particles become hydrophobic. The latter can be broken to reform silanol groups, but in water at room temperature this is a very slow process.

Following this second drying, the behavior of the particles can remain stable for some hours. To maintain the behavior for longer than this the particles need to be stored under an atmosphere of humidity that matches their level of hydration. Since identifying their level of hydration is extremely difficult, we prepared fresh particles for each set of experiments.

2.3. Formation of emulsions

The procedure for making bijels has been described previously [2,32]. A typical mixture was prepared as follows. Silica particles, water and the xanthene dye rhodamine B were mixed and sonicated with a probe (6–8 W, 2 min) and cooled to room temperature. Lutidine was added to give a critical composition water-lutidine binary fluid (28 wt.% lutidine [15]) with 1.5–2 vol.% particles and 5×10^{-6} M rhodamine B. (The influence of varying particle volume fraction on bijel formation [2] and emulsion inversion [33] have been separately investigated.) On phase separation, the dye partitions into the lutidine-rich phase, distinguishing it from the water-rich phase. While the addition of this extra component may cause a small shift in the LCST (34 °C in the pure system), repeated tests with and without the dye have not shown it to affect the structure of the final emulsion.

The binary fluid was decanted into a 1 mm pathlength optical glass cuvette, sealed with a Teflon plug and placed in a custom-built aluminum heating block thermostatted to 40 °C. A 1 cm-diameter hole was bored through the block to allow microscopy to be undertaken; the block was set up on a Biorad confocal microscope fitted with a Nikon 20× ELWD lens. The FITC-tagged particles were imaged using 488 nm excitation (Argon-ion laser) and an HQ515/30 emission filter. The rhodamine B dye was imaged using 543 nm excitation (HeNe laser) and an HQ600/50 emission filter. During phase separation, images were captured at 1.4/s with a line scanning rate of 600 lines/s in order to resolve the process of

spinodal decomposition. High-resolution images (line scanning at 50 or 100 lines/s) were taken once the emulsion/bijel had stabilized. The cuvette was then removed from the block, sheared by manual shaking at approximately 3 Hz for 3–4 s and returned to the block for imaging. During this process the sample temperature did not fall below T_c .

2.4. Characterization

TGA data were collected using a Rheotherm TG 1000 M + thermogravimetric analyzer with Rheometric Scientific Plus V software. The samples were studied in air at fixed temperature in open aluminum oxide crucibles. A heating rate of $25\text{ }^\circ\text{C min}^{-1}$ was used to raise the furnace to the fixed target temperature.

The ^1H solid state NMR spectra were recorded on a Bruker Avance III spectrometer operating at 400.13 MHz for ^1H and a 9.4 Tesla wide bore magnet with a 7 mm HX Bruker probe. The spectral reference was a replacement sample of adamantane at 1.62 ppm. Zirconia rotors were used on all samples with a KELEF drive cap and samples were spun at 6 kHz. A pulse length of 4 μs (62.5 kHz), a repetition delay of 5 s, 16 scans and a spectral width of 120 kHz were used for obtaining the ^1H magic angle spinning (MAS) spectra. The fitting of ^1H spectra was performed using the MestReNova 6.4 software package.

3. Results

3.1. Transitional inversion of pickering emulsions

The particles of primary interest in this work, Fluor-S, are composed of fluorescently labeled colloidal silica. With the correct treatment, they exhibit wetting properties in water–lutidine (WL) mixtures that make them suitable for producing not only bijels but also a suite of emulsion types.

Following their synthesis, washing and initial drying, the silica particles undergo further drying (see Section 2). By varying the temperature and/or duration of this second drying step, the particle wetting properties can be adjusted such that in a water–lutidine system, Pickering emulsions can be formed ranging from L/W to W/L/W (multiple emulsion) to W/L. Transitional inversion of these emulsions is thus achieved by a slight adjustment in the amount of water adsorbed to the surface of the particles.

A confocal microscope is used to track the position and behavior of the particles during phase separation. Rhodamine B dye partitions into the lutidine-rich phase (L-phase), thus distinguishing the two liquid phases, while the particles are fluorescent. The resulting emulsion is observed; the sample is manually sheared (see Section 2) while still in the two-phase region and observed again. This second observation can be compared to the emulsion type that forms spontaneously upon phase separation. After shearing, a droplet emulsion is invariably formed, allowing direct comparison between samples of this particular emulsion type. Note that because of the method of shearing, the droplet size is not well controlled. However, the geometry of the emulsion droplets (spherical or otherwise) is the direct result of the wetting properties of the particles.

Fig. 1 illustrates the behavior of five samples of Fluor-S particles (NB all particles with the same name are from the same synthetic batch). From top to bottom, these were dried for increasing lengths of time (30 min, 70 min, 130 min, 250 min and ~ 10 h respectively). The left column shows confocal images of the emulsions formed immediately after separation; the right column shows the same samples after being sheared. Red indicates the rhodamine B dye and thus the lutidine-rich phase (L-phase); green is the signal from the FITC-tagged particles.

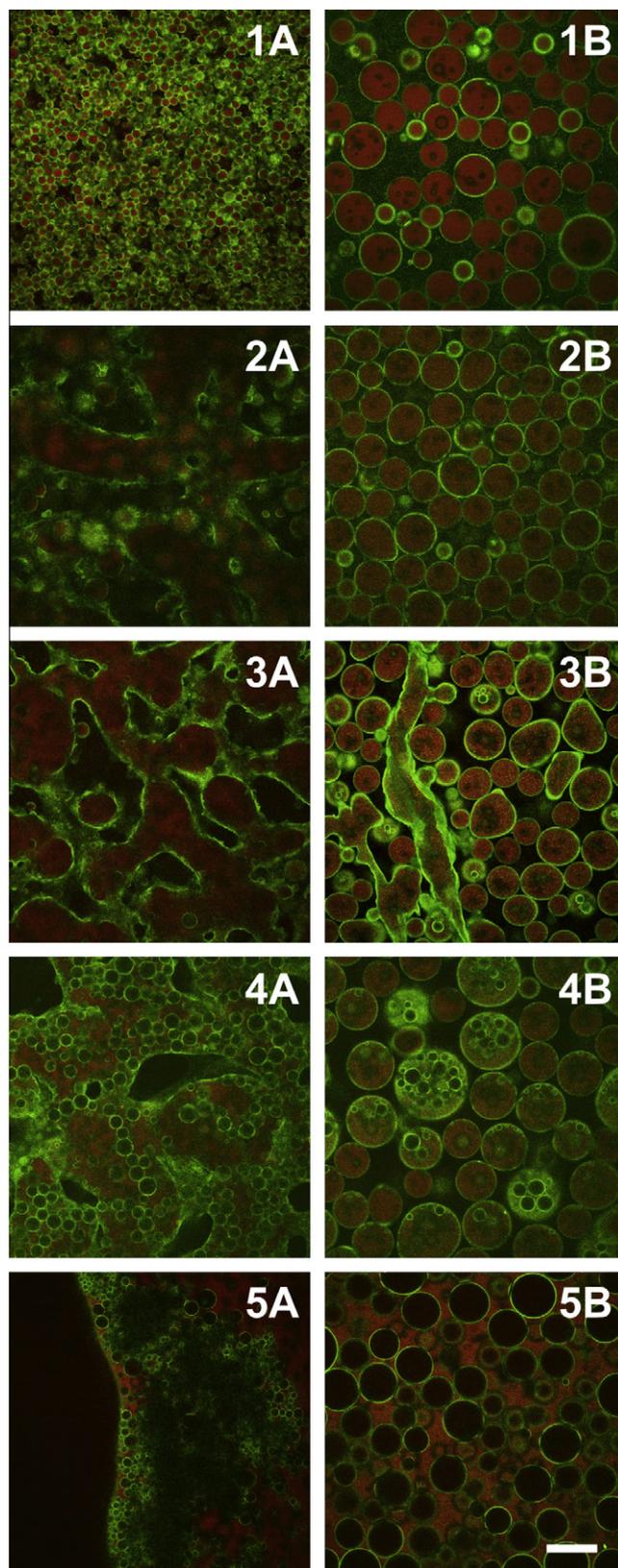


Fig. 1. Confocal microscopy images of emulsions formed by particles dried for increasing lengths of time at $170\text{ }^\circ\text{C}$ (top to bottom 30, 70, 130, 250 min and 10 h). Left column: emulsions/bijels formed by initial separation; right column: the same samples after shearing. (scale bar = $100\text{ }\mu\text{m}$; green = Fluor-S particles, red = lutidine-rich phase labeled with rhodamine B; sample composition: 28 wt.% lutidine-in-water, 2 vol.% particles; $T = 40\text{ }^\circ\text{C}$). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The sample with the least amount of drying forms an L/W emulsion (1A). With a slight increase in drying time (2A), a bijel is formed, but note that the W-phase within the bijel is an L/W emulsion. This is the result of secondary nucleation during spinodal decomposition.

During the formation of a bijel, the fluid domain size increases as spinodal decomposition progresses. Secondary nucleation then occurs, with droplets of L-phase forming in the W-phase domains, and droplets of W-phase in the L-phase domains. If the fluid domains are free of particles, these droplets migrate to join a domain composed of their own fluid phase. However, if excess particles are present in either of the domains, these particles attach to and stabilize the newly formed droplets. In the case of 2A, while most particles in this sample had sufficiently neutral wetting to attach to the interface during spinodal decomposition (allowing the interface to jam and the bijel to form), some remained dispersed in the W-phase and stabilized L-phase droplets.

On shearing (1B and 2B), these two samples both form L/W emulsions. Several droplets are visible in 2B that are not perfectly spherical: an indication that the average contact angle of the particles is closer to 90° and can support surfaces of lower curvature. Note that in both images the W-rich phase appears slightly green, indicating some particles are dispersed in that phase. Along with the Pickering droplets inside the 2A bijel, this is evidence of slightly non-uniform wetting properties in the particle sample. This is because of the near impossibility of achieving perfectly even drying for a given sample; in clusters and clumps of particles, some particles will inevitably lose slightly more water than others.

The third sample formed from drying particles for 130 min (3A) forms a good bijel, indicating the particles have an average contact angle of 90° and a relatively narrow distribution about this average. On shaking (3B), the emulsion is still L/W, but a significant number of non-spherical droplets and tube-like droplets form, and a small proportion of the particles are dispersed in the L-phase. Whether the tubes are remnants of bijel that have not been fully dispersed, or form as a result of shearing during shaking is unknown, but in many samples the tubes continue to re-appear after repeated shaking.

The fourth sample (4A) has been dried further, and forms the inverse of sample 2: a bijel in which the L-phase is a W/L emulsion. This sample has a slight average preference for the L-phase, and shaking causes a double emulsion of W/L/W to form (4B). For this to occur, sufficient numbers of 'dry' particles must be present to stabilize the small W/L droplets while there still remain enough 'wet' ones to stabilize the larger L/W globules.

The final sample (5A), having had the most drying, has a clear preference for the L-phase. The initial result of separation is a macroscopic separation of the two phases, giving a W/L emulsion with excess bulk W-phase. The latter contains no particles. On shaking (5B), a W/L emulsion forms, with no non-spherical droplets and a significant proportion of particles dispersed in the L-phase.

All the emulsions in this work were made at the WL critical composition of 28 wt.% lutidine, so phase separation proceeds by spinodal decomposition. This route is reflected in the structure of the bijels formed by particles with neutral wetting. Using the confocal microscope, particle wetting properties can be identified very early during spinodal decomposition by their location in the separating mixture (W-phase, L-phase or interface). In all cases for the Fluor-S particles, the preference observed during spinodal decomposition correlates with the final emulsion formed. For instance, if the particles are largely located in the water-rich phase during spinodal decomposition, the final emulsion will be L/W. If instead the particles show a strong and early attachment to the interface during spinodal decomposition, the final result will be a bijel. This appears to be a colloidal analog of Bancroft's rule, which applies to molecular emulsifiers, and states that the phase in which the emulsifier is more soluble will tend to become the continuous phase.

3.2. Hydration of the particle surface

It is clear that small adjustments to the drying conditions of the Fluor-S particles are enough to significantly alter their wetting behavior in the water–lutidine system. This is particularly noticeable when the contact angle is close to 90°. This sensitivity to drying has in the past caused us some confusion by producing contradictory emulsion behavior after apparently identical drying.

The temperatures at which the particles are dried are low enough that little chemical change must occur to the silica surface itself. Temperatures of 180 °C for durations of longer than an hour are sufficient for a proportion of the surface silanol groups to condense to form siloxanes [19]. However, if drying is performed at lower temperatures and/or for shorter times, particles which have been over-dried and display a clear preference for the L-phase can be returned to a W-phase preference by soaking in water. This drying/rehydration cycle can be performed numerous times, allowing the particles to be re-used.

Given these observations, the determining factor in the wetting behavior of these particles is almost certainly the amount of water adsorbed to the silica surface. In an attempt to quantify this relationship, we analyzed the particles using thermogravimetry and NMR spectroscopy.

Fig. 2 shows four thermogravimetric isotherms of particles dried at 70 °C, 100 °C and 180 °C (two batches). Mass loss occurs in two stages, the first lasting around 5 min (note that the TGA oven is still approaching constant temperature during this time). The majority of the mass is lost in this stage, and the point at which the rate of loss begins to level off depends on the temperature. Since water bound to the surface of silica is likely to exist in a variety of configurations and with hydrogen bonds of varying strengths [19], increasing the drying temperature will remove more of it in this first stage.

During the second stage, there is incremental mass loss for an indefinite period of time. While Fig. 2 shows only the first hour of drying, we followed the slow loss of mass by TGA for nearly 24 h. Whether this is water making its way out of pores in the silica mass or the slow rearrangement and loss of water bound at the surface is unclear. In one instance, particles dried in our regular oven and tested for emulsion behavior at regular intervals reached the point of neutral wetting after 112 h of drying at 100 °C. Given the shallow gradient of the isotherms above, there could only have been a minimal difference in the amount of bound water after, say, 96 and 112 h drying. Nevertheless, in that period, the sample had improved from forming an L/W emulsion with a few bijel-like walls, to forming a symmetric bijel.

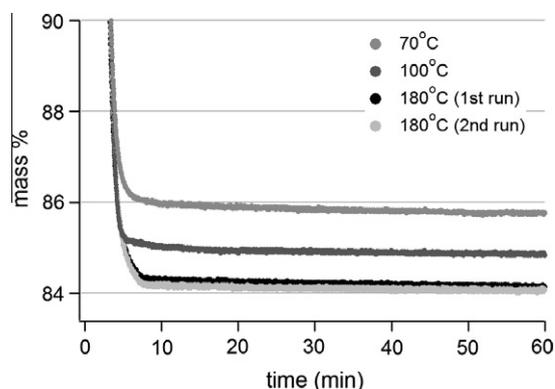


Fig. 2. Thermogravimetric isotherms showing loss in mass over time performed on Fluor-S particles at three temperatures. Particles had initial drying overnight at 30 °C. All four experiments are still gradually losing mass at 60 min and beyond. Note the difference between the two samples dried at 180 °C.

In addition to the obvious factors of temperature and drying time, the wetting behavior is so sensitive that the depth of the particle layer or the size of particle clumps during drying can make the difference between a preference for one phase or the other. Note the difference in Fig. 2 between the two samples dried at 180 °C. The initial masses of these two 7 mg samples differed by only 1%, but they have slightly different relative mass losses, perhaps due to some packing variation in the TGA crucible. In this case, with such small samples, the relative mass loss eventually converged at around 24 h, but for the larger samples and shorter drying times used in our emulsion experiments this is not necessarily the case. Such samples, though treated in an apparently identical fashion, will then exhibit different emulsion behavior.

Five batches of Fluor-S particles were dried and tested for emulsion behavior, and then analyzed by ^1H MAS-NMR (Fig. 3). The wettest sample (a) had received only the initial low-temperature drying. Unlike the thoroughly dried samples, this powder does not flow freely but is instead slightly 'sticky' and shows a broad inhomogeneous signal that we attribute to a significant amount of physisorbed water at different sites on the surface of the silica. Particles that have been dried at higher temperatures (200 °C for 2 h, in this case), such that they cannot be fully re-hydrated and form only W/L emulsions, show a complex peak (e) that indicates significant change to the silica surface. This is likely to be due to the dehydration reaction of silanols into siloxane bonds [20].

In contrast, the three intermediate samples (b–d) all show a relatively narrow peak at around 3.7 ppm, with a broad downfield shoulder. These three samples underwent similar drying treatments and all have some ability to make bijels: b (dried for 55 min at 170 °C) makes a well-proportioned bijel with very little secondary nucleation, while c (45 min at 170 °C; this was a smaller sample and dried more quickly) and d (75 min at 170 °C) are on the drier side and show some secondary nucleation in the L-phase.

In all three cases, the spectra can be deconvoluted (Fig. 4) into a combination of a broad peak at around 5 ppm and a narrower peak at 3.5–4 ppm. Table 1 shows the relative areas of these fitted peaks. We attribute the broad peak to hydrogen-bonded silanol groups on the surface of the silica, and the narrower peak to physically adsorbed water molecules [34,35]. Note that the relative area of the narrower peak decreases for the drier samples, indicating that

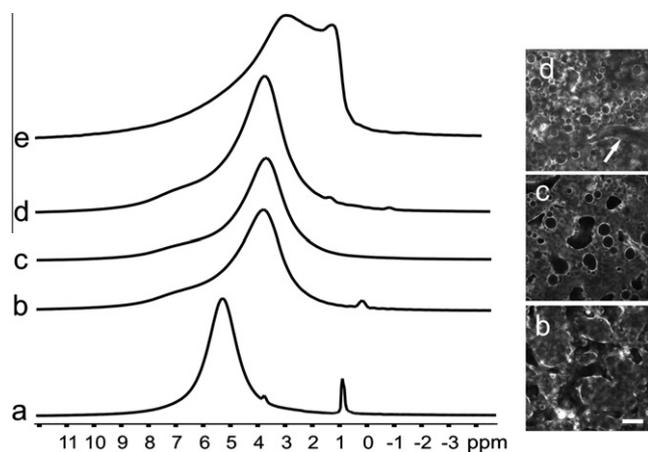


Fig. 3. ^1H MAS-NMR spectra from five samples of Fluor-S particles. From bottom to top, the samples were dried for increasing lengths of time and exhibit an increasing preference for the L-phase. The inset images show bijels formed by samples (b–d). Sample (a) forms an L/W emulsion; (b) forms a bijel; (c) forms a bijel with some L-phase nucleation; (d) forms a very asymmetric bijel (inset shows mostly W/L emulsion, with arrow indicating bijel-type domain); (e) is an 'over-dried' sample that cannot be easily re-hydrated, and forms W/L emulsions only. Scale bar = 100 μm . The small sharp upfield peaks in (a), (b) and (d) were identified as contaminants in the rotor.

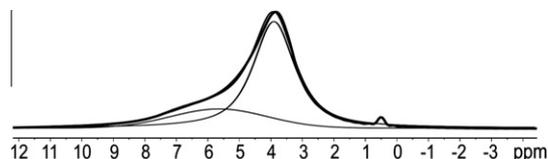


Fig. 4. Example of the deconvolution of ^1H solid state NMR data from samples a–d in Fig. 3. Each spectrum is fitted by two peaks, with the narrower upfield peak attributed to physisorbed water, and the broader downfield peak to hydrogen-bonded silanol groups.

the amount of surface-bound water is decreasing. Sample a, which forms L/W emulsions only, can be fitted by a single narrow peak, suggesting that the dominant signal is from adsorbed water. This peak is downfield of the corresponding physisorbed water peaks in the other samples, suggesting the water structure in this wetter sample more closely reflects that of bulk water. We see no sign of a peak suggesting isolated silanols in samples a–d [34,36], but this may be the result of more thorough hydration prior to drying.

3.3. Effect of exposing the particles to lutidine

Early in the development of WL bijels we observed that if the same sample was subjected to repeated cycles of heating (phase separation) and cooling (re-mixing), the wetting preference of the particles moved gradually towards the L-phase [32].

This shift is in fact a general feature caused by exposure to lutidine, with particles dispersed in lutidine or in WL mixtures undergoing a slow drift in wetting properties that mirrors the change that occurs as drying times are increased. For instance, after exposure to a critical concentration of WL mixture for 1 week, particles with minimal drying (initially forming only L/W emulsions) had achieved neutral wetting (i.e. they formed a bijel). After continued exposure they showed a preference for the L-phase. This change occurs more quickly if a sonic probe is used on the dispersion.

3.4. Effect of modified silica surface on particle wetting properties

The experiments described in the previous sections were performed using the Fluor-S particles. In synthesizing these particles, a mixture of APTES and APTES-FITC is added (see Section 2) and both these compounds become covalently linked with and evenly distributed throughout the volume of each particle. They are thus present on the surface of the particles, with a proportion of the surface silanols being replaced by FITC molecules and aminopropyl groups.

To help determine the effect of these surface species on the emulsion behavior with these particles, we made a comparison with particles having an unmodified silica surface (Fig. 5). These particles (designated Plain-S) have a fluorescent core (chemically identical to the Fluor-S particles) covered by a shell of pure silica. They are visible by confocal fluorescence microscopy, but have neither APTES nor FITC on the surface. Pictures in the left column of Fig. 5 were acquired during spinodal decomposition. A slight temperature gradient in the cuvette causes phase separation to move as a front across the field of view from bottom right to top left; this combined with the finite speed of the confocal line scanning has resulted in the top left of each image showing an earlier stage of spinodal decomposition than the bottom right. Pictures in the right column were acquired after phase separation was complete and no further change was occurring to the emulsion structure.

With minimal drying, the Plain-S particles behave like similarly treated Fluor-S particles. During spinodal decomposition they remain dispersed in the W-phase, and the end result is an L/W emulsion (Fig. 5, 1A/B). A notable difference does exist in the emulsion

Table 1
Data from the deconvolution of peaks a–d in Fig. 3.

Sample	Physisorbed water			H-bonded silanol groups		
	Shift (ppm)	Relative area (%)	Linewidth (Hz)	Shift (ppm)	Relative area (%)	Linewidth (Hz)
A	5.28	100	506	–	–	–
B	3.78	74	607	5.31	26	1356
C	3.72	62.4	589	5.12	37.6	1517
D	3.74	62.1	575	4.95	37.9	1592

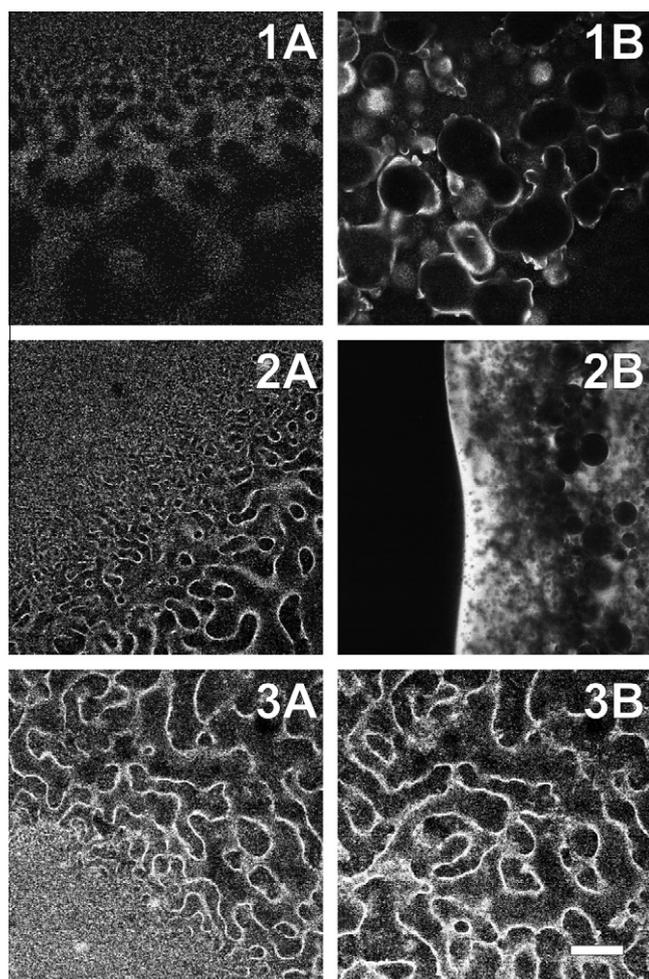


Fig. 5. Comparison of the behavior of Fluor-S and Plain-S particles (particle signal only; no rhodamine B labeling in the fluid phase). Left: images acquired during spinodal decomposition; right: final emulsion structure. Top pair: spinodal decomposition of Plain-S with strong preference for W-phase (1A) and resulting L/W emulsion with excess particles in the W-phase (1B). Middle pair: spinodal decomposition of Plain-S with neutral wetting (2A), and resulting phase separation with excess particles in the L-phase (2B; W/L with excess W). Bottom pair: spinodal decomposition of neutrally wetting Fluor-S (3A) and resulting bijel (3B). (scale bar = 100 μm).

morphology: whereas Fluor-S particles generally produce spherical or off-spherical droplets, the Plain-S particles stabilize oddly shaped droplets that appear to have been formed by the incomplete fusion of smaller droplets. With further drying, Plain-S particles produce a W/L emulsion, indicating that transitional inversion is possible. However, the details show considerable variation from the behavior of Fluor-S particles.

After undergoing the same washing and drying procedures as the Fluor-S particles, samples of Plain-S were dried such that most particles attached to the interface during spinodal decomposition

(Fig. 5, 2A). However, we found that when phase separation was complete, the result was neither a bijel nor a droplet emulsion stable to coalescence, but complete separation of the two phases, with most particles ending up in the L-phase (2B). Fluor-S particles attaching to the interface during spinodal decomposition (Fig. 5, 3A) always result in a bijel (3B); in contrast, the Plain-S particles have never been observed to form a bijel.

An insight into the unexpected behavior of the Plain-S particles can be gained by tracking the location of the particles during spinodal decomposition. Fig. 6 shows a spinodal decomposition snapshot of a sample containing Plain-S particles having a slight preference for the W-phase. The confocal data are split: the left image shows the particle signal, the right image the signal from the rhodamine B dye, which distinguishes the L-phase (bright) from the W-phase (dark). As in Fig. 5, a temperature gradient has resulted in the top left of each image showing an earlier stage of spinodal decomposition than the bottom right.

In the early stages of spinodal decomposition, some particles are visibly dispersed in the W-phase while the rest have attached to the liquid–liquid interface. In the particle image (left), as spinodal decomposition progresses, the bright interface line is seen to blur and the L-phase to brighten. No obvious change is seen in the brightness of the W-phase. Our tentative interpretation of these data is that while little change occurs in the concentration of particles in the W-phase, those particles that are attached to the interface leave it and disperse into the L-phase. (Note that the final result of this separation was very similar to image 2B in Fig. 5, showing complete separation.)

It is evident that neutrally wetting particles that initially adsorb to the interface change their wetting properties in the course of spinodal decomposition to almost completely preferring the L-phase. However, this shift is largely reversible: if the sample is cooled, re-mixed and then re-heated to cause a second phase separation, the particles show the same initially neutral behavior, first attaching to the interface and then dispersing into the L-phase. (Over multiple cycles and hence a lengthy exposure to lutidine, the particles will show a slow drift towards a preference for the L-phase, as discussed above.) Fig. 7 illustrates a cycle of this kind. In the early stages of spinodal decomposition (1A), the particles are again distributed between the interface and the W-phase. The end result (1B) is complete separation, with most particles in the L-phase and a small proportion stabilizing lutidine droplets in the W-phase. When the sample is cooled and re-heated, spinodal decomposition proceeds as before (2A), and the final result (2B) is similar to the first (though no L/W droplets are visible in this image). Clearly, the sudden change in wetting properties that occurs during phase separation is easily reversed upon re-mixing.

This gulf in behavior between the two types of particle – modified silica and bare silica – must in some way be due to the presence of APTES and APTES-FITC on the surface of the Fluor-S particles. In order to probe this further, we synthesized a further type of particle.

Amino-S is a non-fluorescent analog of Fluor-S. The same concentration of APTES is used in the synthesis but no FITC dye is added, meaning the only non-silica groups on the surface are aminopropyl groups. The lack of fluorescence in these particles made it

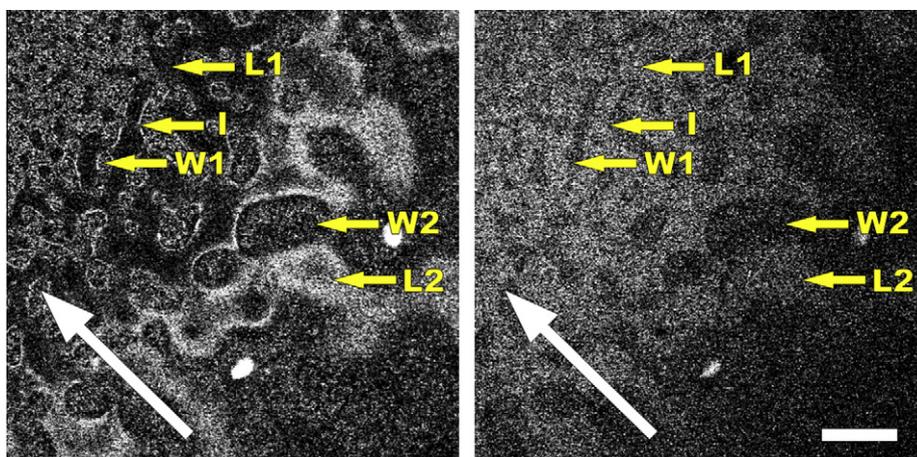


Fig. 6. Snapshot taken during spinodal decomposition of a mixture containing Plain-S particles, with confocal signals from the particles (left) and dye (right) separated. The L-phase appears brighter in the dye image. Spinodal decomposition is progressing in the direction shown by the large white arrows. Arrows marked L, W and I indicate the L-phase, W-phase and interface respectively. Note that early in spinodal decomposition (W1, I, L1) particles are visible in the W-phase and at the interface, but not in the L-phase. Later on, particles at the interface disperse into the L-phase (L2), while the density of particles in the W-phase remains constant (W2). (The two small bright spots in the image are undispersed clusters of particles. These clusters show up in the dye image not because rhodamine has adsorbed to them, but because they are intense enough that the emission wavelengths of the FITC 'leak' into the detection range of the dye-signal photomultiplier tube.) (scale bar = 100 μm).

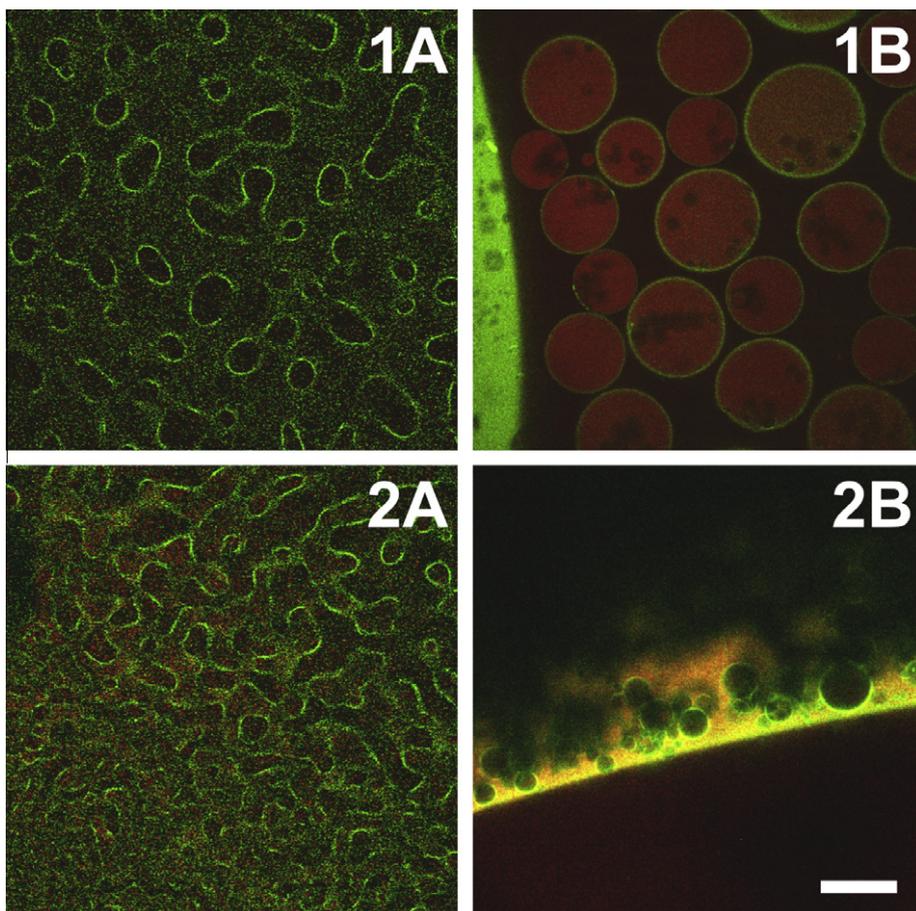


Fig. 7. Repeated separations of Plain-S particle-stabilized systems with near-neutral wetting. (1A) snapshot of spinodal decomposition; (1B) resulting emulsion (W/L on left, some L/W on right); (2A) same mixture during second spinodal decomposition; (2B) resulting emulsion (W/L with excess W). (scale bar = 100 μm).

more difficult to resolve their behavior during spinodal decomposition (reflection rather than fluorescence was used), but the end result was clear. Once particles attach to the interface, they remain there, meaning Amino-S is able to form bijels like Fluor-S particles. The presence of FITC on the surface is therefore not crucial.

4. Discussion and conclusion

In a system consisting of the water–lutidine binary fluid with colloidal silica particles, we observe two distinct forms of behavior. First, the wetting properties of the particles are strongly dependent

on the way in which they are dried, and this dependence can be used to effect a transitional inversion in water–lutidine mixtures. This dependence is a non-equilibrium property, and can be overcome by long exposure to the binary fluid mixture. Second, the type of emulsion formed on phase separation – specifically whether or not bijels form – depends on the surface chemistry of the particles.

In the first case, we observe that by simply changing the amount of drying to which the modified silica particles (Fluor-S, Amino-S) are exposed, we can cause transitional inversion in the WL emulsion stabilized by the particles. As we increase the amount of drying, the emulsion formed varies from a L/W droplet emulsion to a bijel to a W/L droplet emulsion. When the same samples are shaken by hand after the initial separation, a variation from a L/W emulsion with spherical droplets, to a L/W emulsion with off-spherical droplets, to a W/L/W multiple emulsion to a W/L emulsion is seen. This continuum of behavior is due to varying amounts of water bound to the surface of the particles.

Water interacts with silica via hydrogen-bonding with the silanol groups [19]. Lutidine is known to adsorb strongly to silica, and 2,5-lutidine and 2,4,6-dimethylpyridine have been shown to adopt a face-on configuration to the silica surface, with bonding occurring between the bridging oxygen in siloxane bonds or deprotonated silanol groups and the aromatic π -system of the pyridine derivative [22,23]. It is reasonable to assume that the same bonding occurs for 2,6-lutidine.

Bare or partially hydrated silica surfaces are primarily covered with deprotonated silanol groups and may also have some siloxane bonds exposed to the bulk solvent [19,20]. Removing some or all of the adsorbed surface water from silica particles thus favors the bonding of lutidine and the preference of particles for the L-phase. Such particles form W/L emulsions. By contrast, when sufficient water is bound to the silica surface, the silanol groups and the siloxane bonds are masked, making the particles appear less like silica and more like water: the surface then shows a preference for the W-phase.

We suggest that the balance between physically adsorbed water and exposed silanol and siloxane groups probably controls the wetting properties of the particles in this system. By varying the drying conditions, one may navigate between the extremes of water-free, silanol-rich (with additional siloxane groups) silica, and water-shrouded silica. At some happy medium, particles are produced that are wetted equally by the two phases and that form structures such as bijels and double emulsions.

We emphasize that when the particles are close to neutral wetting, their emulsion behavior shows an extreme sensitivity to the amount of surface water. Particles treated in a very similar fashion can display a large variation in bijel appearance, and apparent inconsistencies in drying times relative to bijel behavior have often been observed. Consider the samples analyzed by solid state NMR (Figs. 3 and 4). The trend in bijel appearance does not match the actual length of time for which the samples were dried. The reason for this is that the mass of particles dried was different in each case; variations in drying within each sample are likely to play a part. Siloxane bridge formation is known to be catalyzed by water vapor [19]; behavior which makes the system very sensitive to the thickness of the powder layer and the presence or absence of a vacuum. Nevertheless, the NMR results show the same trend as is observed by confocal microscopy, affirming the link between adsorbed water and emulsion behavior.

The adsorption of lutidine at the silica surface is also an important factor. When fully hydrated particles are exposed to lutidine or a WL mixture for some period of time prior to the emulsion being formed, their wetting preference moves from the W-phase to the L-phase. In this case, we believe the bound layer of water at the surface of the silica gradually equilibrates with the sur-

rounding solvent, with water molecules becoming replaced by lutidine molecules. At some point, particles with an initial preference for the W-phase have adsorbed sufficient lutidine to show a preference for the L-phase. This equilibration is a relatively slow process, and the wetting behavior of particles in a water/lutidine mixture can change very little over time scales of a few hours. If this equilibration were fast, we would not observe different behavior from differently dried particles: no matter what the initial condition of the particles, the bound solvent layer would equilibrate with the bulk solvent mixture before the emulsion was formed and all the samples would show the same emulsion results.

While solvent adsorbed to the particle surface moves the particle behavior along a continuum, the surface chemistry of the particles themselves appears to cause a step-change. Unlike the modified silica particles (Fluor-S and Amino-S), the surfaces of which are partly covered with combinations of APTES and APTES-FITC, we have never observed particles with an unmodified silica surface (Plain-S) to form bijels. This is due to a second process that occurs to unmodified silica early in phase separation and which rapidly shifts its wetting behavior towards a preference for the L-phase. As spinodal decomposition proceeds, any Plain-S particles that initially attach to the interface are later seen to detach from the interface and disperse into the L-phase. Jamming never occurs and no bijel results. Those particles that start in the W-phase and never reach the interface remain in the W-phase.

Plain-S particles that initially attach to the interface during spinodal decomposition have neutral wetting and have probably formed a surface layer of water and lutidine. Further lutidine may then associate (possibly via aromatic π -stacking interactions) with the bound lutidine. This leads the particles to become enveloped by a wetting layer of the L-phase and they then disperse into it (leaving the interface). In contrast, particles that initially disperse in the W-phase do so because they have a greater proportion of surface-bound water. This prevents them from adsorbing lutidine over the timescale of the separation and they do not become wetted by the L-phase.

Minimally dried Plain-S particles universally partition into the W-phase; they do not attach to the interface, do not acquire a wetting layer of the L-phase and the result is an L/W emulsion. Nevertheless, the odd shapes formed in this latter case (Fig. 5; 1B) suggest that some slight change in wetting properties has occurred: enough, at least, to cause jamming when two droplets coalesce. This may reflect the presence of lutidine in the W-phase, which may change the surface characteristics. It is also possible that as the interfacial tension increases, the driest particles in these wet samples attach to droplet interfaces just in time (i.e. at a temperature just low enough) to acquire a partial wetting layer.

Importantly, the timescale of this process (tens of seconds) is substantially different to that required to modify the adsorbed layer of water (~hours). Hence we assume that it involves the formation of a temporary wetting layer rather than any extensive accumulation of a surface-bound layer. This would explain why upon cooling and re-mixing the phases, the particles return to their original wetting behavior. The question remains as to why Fluor-S and Amino-S particles do not behave like this. Amino-S particles demonstrate that the presence of FITC is not crucial, and that the determining factor must be the aminopropyl groups on the silica surface. If the formation of the wetting layer relies to some extent on π -bonding – either between lutidine and deprotonated silanol groups (or bridging oxygen atoms) or between surface-bound and solvent lutidine molecules – then the presence of the protruding aminopropyl groups could disrupt this short-range bonding. In addition, the existence of these groups will reduce the density of both silanol groups and siloxane bridges. We know that Fluor-S particles do adsorb lutidine over long timescales, so the silica–lutidine association is not prevented, but it may be sufficiently hin-

dered that the wetting layer is not able to form on the short time-scale of our experiments. The particles therefore remain at the interface until jamming occurs and the metastable bijel state is achieved.

In a previous study [32] we began investigating the interaction between the modified silica surfaces and the water–lutidine system. We systematically varied the concentration of dye (fluorescein isothiocyanate) used to prepare the particles, finding that with increasing dye loading, the particle surfaces become more hydrophilic. This was established via observations of transitional inversion from a water-in-lutidine emulsion via a bijel to a lutidine-in-water emulsion. We also observed that, with thermal cycling, the surface properties changed. With continued exposure to water–lutidine mixtures the hydrophilic particles (high dye concentration) lost their initial preference for the water-rich phase. Based on the variation of wetting with dye concentration and related studies from the literature we tentatively concluded that the key ingredient was the 3-(aminopropyl)triethoxysilane (APTES), which is added when the dye is added, changing the surface coverage of amino groups. Increasing the proportion of amino groups (replacing silanol groups) appears to increase the preference for the water-rich phase. At that time we suggested that the surface silanol groups might adsorb to the lutidine molecules via electrostatic interactions and hydrogen bonding with the nitrogen lone pair. It is more likely that the interactions will occur via π -bonding between the lutidine ring and either the oxygen of a surface siloxane or deprotonated silanol group. Replacing these surface groups with amino moieties would therefore reduce lutidine adsorption, making the surfaces increasingly hydrophilic.

Pickering emulsions (currently) and bijels (possibly) can be employed in commercial emulsion and gel applications. Pickering emulsions are robust and versatile and avoid molecular surfactants which are sometimes unpopular with consumers. The bijel has a geometry which might allow it to be applied in co-release [3] or co-flow applications [37]; it might also be employed as a porous medium [7,10] as a tissue scaffold or in a broad range of other applications. To fully exploit these technologies much must be learnt about bulk production and about tuning the properties. Our understanding of the particle surfaces presented here is only the first step. One point of great interest is the aging behavior of the bijel as the particle size becomes very small [38] – which could be pertinent in some application areas.

Acknowledgments

We gratefully acknowledge productive discussions with and expert assistance from Job Thijssen and Sylvia Williamson. Funding

in Edinburgh was provided by Scottish Enterprise SE/POC/8-CHM-002.

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