

Particle stabilised emulsions studied by WETSEM technique†

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We have developed a new simple method to study the interfacial structure of particle stabilised emulsions *in situ* by wet scanning electron microscopy (WETSEM) technique for the first time. Particle layer(s), particle location, aggregation and bridging interaction were clearly observed with very high resolution in a range of solid particle stabilised emulsions.

There has been a significant resurgence of interest in particles adsorbed at liquid–gas and liquid–liquid interfaces, particularly in relation to their stabilisation of foams and emulsions.¹ For particle-stabilised emulsions with equal volumes of oil and water, the main determinant of emulsion type is the contact angle θ .² For θ measured through water, when θ is $< 90^\circ$ (corresponding to a hydrophilic particle) the adsorbed particles protrude more into the water phase, which creates a tendency for the adsorbed particle film to curve such that oil-in-water (o/w) emulsions are formed. When $\theta > 90^\circ$ (corresponding to hydrophobic particles) the situation is reversed and w/o emulsions are formed. Scanning microscopy techniques have been developed, largely in the past few decades,^{3,4} driven by the ever increasing demand for imaging at smaller and smaller scales, far below the resolution of optical microscopy. Electron microscopy has been used to investigate the structure of surfactant-stabilised emulsions.⁵ Oza and Frank,⁶ employing freeze-etch transmission electron microscopy (TEM), studied the properties of o/w emulsions stabilised by microcrystalline cellulose particles. Low temperature field emission scanning electron microscopy (LTFSEM) was used to observe the interfacial structure around drops in solid stabilised emulsions.⁷ Generally, light microscopy, TEM and SEM techniques have some limitations: the resolution of light microscopy is limited by diffraction to $0.25\ \mu\text{m}$; the use of TEM is encumbered by extensive processing of the sample, which may alter its structure significantly; SEM requires specialized preparatory techniques such as fracturing, etching, fixation and coating.

Unlike all the above studies, we have used WETSEM technology⁸ to characterise the interfacial structure of solid stabilised emulsions without any treatments. The WETSEM technology is a technology which enables direct imaging of fully hydrated samples in scanning electron microscopes. This technology is based on a thin, electron-transparent membrane, which seals the sample from the vacuum in

the microscope chamber and it is strong enough to sustain a 1 atmosphere pressure difference. The membrane is made from a polyimide polymer of 145 nm thickness and allows the penetration of electrons and the collection of backscattered electrons. It is worth mentioning that environmental scanning electron microscopy (ESEM) enables wet samples to be observed but only the top layer of the sample surface is revealed.⁹ The WETSEM differs from ESEM mainly in that it can be applied to any SEM and enables observation of liquid samples that are a few microns deep. We used QX-102 capsules (Quantomix Ltd.) for WETSEM emulsion characterisations (Fig. 1). The QX-102 capsules (consisting of a liquid dish and a sealing stub) can be used for imaging various wet materials and biological samples. Utilising a suitable SEM detector, the contrast between water and oil is especially well visualized with WETSEM technology, enabling us to analyse the behaviour of solid particles at curved liquid–liquid interfaces for the first time in emulsion samples. Samples in liquid form can be imaged directly simply by placing them inside the QX-102 capsule. The sample preparation is comparable to light microscopy, and no drying, coating or embedding steps are required. The emulsion samples were imaged without any treatment. The dish of the QX-102 capsules was filled with $15\ \mu\text{L}$ of the desired emulsion sample and then closed tightly. Here we describe the procedure in more detail.

Tricaprylin 812N (min 99%, from Sigma), a medium chain triglyceride, was used as an oil phase. For the emulsions prepared in this study we used different sizes of hydrophobic silica particles (Microparticles GmbH, Germany) or monodisperse surfactant-free white aliphatic amine polystyrene (PS) latex particles (IDC, USA). The silica particles have diameters of 519 nm, 988 nm and $2.2\ \mu\text{m}$ modified with hydrophobic groups (C18) per particles surface of 8.4×10^{-13} , 1.7×10^{-13} and $5 \times 10^{-13}\ \text{mM}\ \mu\text{m}^{-2}$ respectively. The

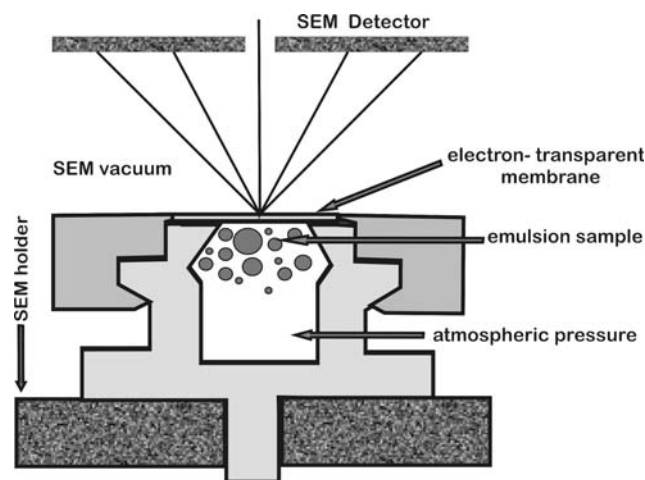


Fig. 1 A schematic of a QX-102 WETSEM capsule.

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† Electronic Supplementary Information (ESI) available: WETSEM and optical images and additional experimental details, and a video of solid particles at liquid–liquid interfaces. See DOI: 10.1039/c0sm00032a/

tricaprylin-in-water (o/w) emulsion with oil volume fraction ($\phi_o = 0.17$) was stabilised by 1 or 2 wt% hydrophobic silica particles initially dispersed in water with the help of an isopropanol-ethanol (1 : 1) mixture. The desired amount of silica particles were dispersed in 0.5 g of the aqueous phase by sonication for 1 min at 10% power using a Branson digital sonifier (450 W, 20 KHz) then 0.1 ml of oil was added to the silica dispersion and homogenisation started by passing the system through a syringe and needle (0.6×25 mm) for 7 to 10 passes. Emulsion samples were imaged by optical microscopy using an Olympus BX-51 (fitted with a DP70 digital camera). For the water-in-tricaprylin (w/o) emulsion ($\phi_w = 0.17$), 1 wt% of silica particles were dispersed initially in the oil phase (0.5 g), then 0.1 ml of pure water was added and the system was homogenised in a similar way as above. Latex particles were dispersed from their original aqueous dispersions into the water phase containing 1.6 wt% NaCl (min 99.9%, BDH) to improve particle attachments to the oil–water interface. After filling the QX-120 capsules (Fig.1) with the emulsion samples, we studied their structure and behaviour using SEM (Carl Zeiss SMT Ltd, Model: EVO 60) applying a solid-state 4-quadrant backscattered electron detector (BSE) in normal high vacuum mode.

Initially, we used an electron gun voltage of 20 KV, subsequently increased to 25 KV. Also, an electron beam probe current of initially 200 pA, subsequently increased to 500 pA was used.

Fig. 2a-d present SEM images of tricaprylin-in-water (o/w) emulsions ($\phi_o = 0.17$) stabilised by different concentrations of 988 nm hydrophobic silica particles. It is evident from Fig. 2a and b that most of the silica particles are immersed in the oil phase, which was expected as they are hydrophobic. Using BSD during the SEM examination, we were able to distinguish between the oil phase (the dark drop) and the water continuous phase (grey area) and the solid particles (white spheres). We noticed also that a particle monolayer appeared as a rim surrounding the oil drop and few aggregates were seen inside the oil phase. Surface coverage of a dense layer of silica particles around an oil drop can be clearly observed when increasing particle concentration to 3 wt%, as shown in the captured SEM images in Fig. 2c and d for an o/w emulsion droplet with a diameter of ~ 70 μm . A closer look at the droplet top surface revealed that it is covered with a dense monolayer (Fig. 2d) which can act as a steric barrier between the droplets thus preventing coalescence. We also noticed that this monolayer was not perfectly ordered as previously

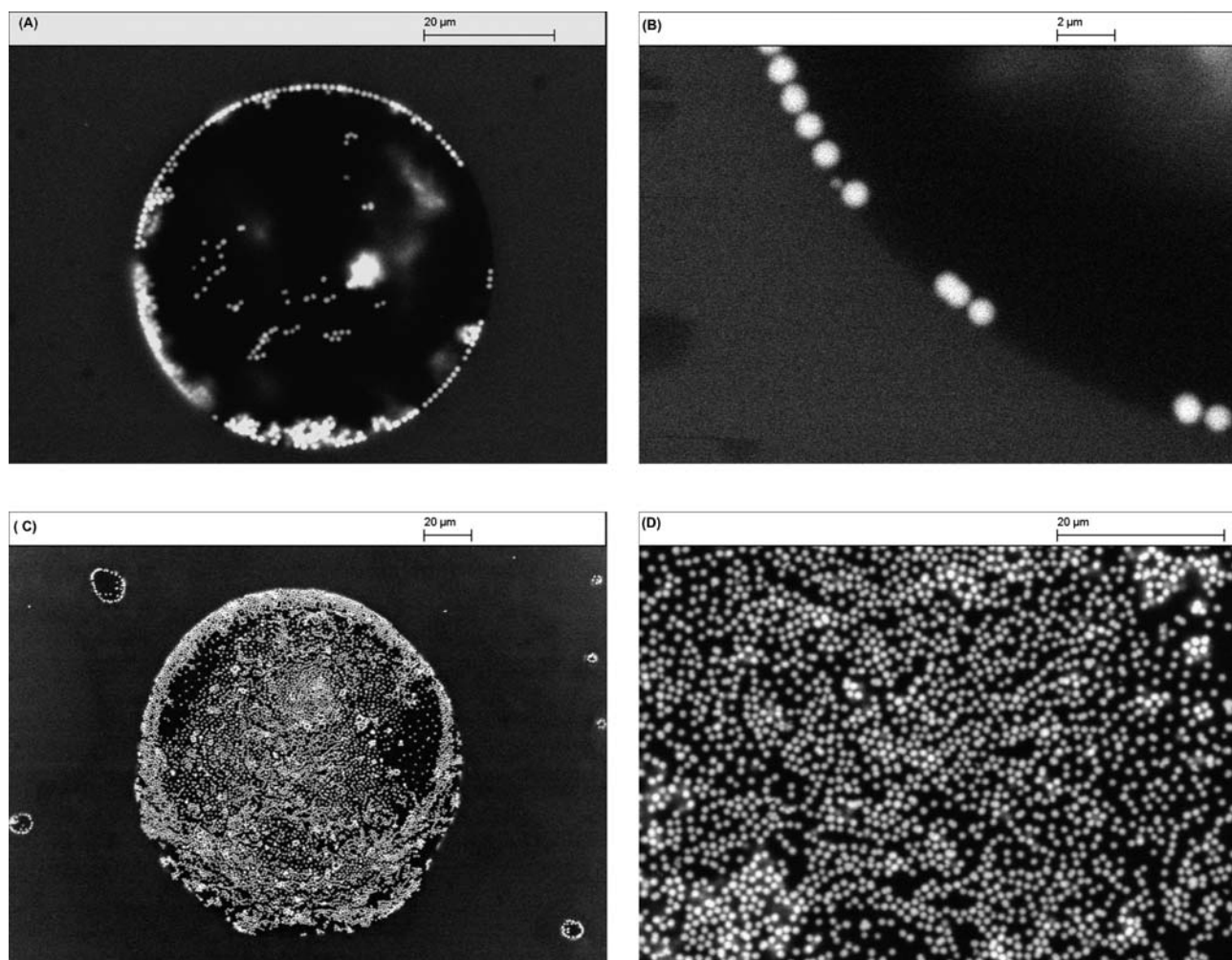


Fig. 2 SEM images of tricaprylin-in-water (o/w) emulsions ($\phi_o = 0.17$) stabilised by 988 nm hydrophobic silica particles. (A) An oil drop of an emulsion stabilised by 1 wt% silica particles. A particle monolayer around the drop is clearly seen. (B) A close view of another oil drop of the same emulsion showing particle location at the oil–water interface where most of the particles are immersed in oil. (C) An oil drop of an emulsion stabilised by 3 wt% silica particles. (D) A particle monolayer adsorbed on the middle of an emulsion oil drop as in (C).

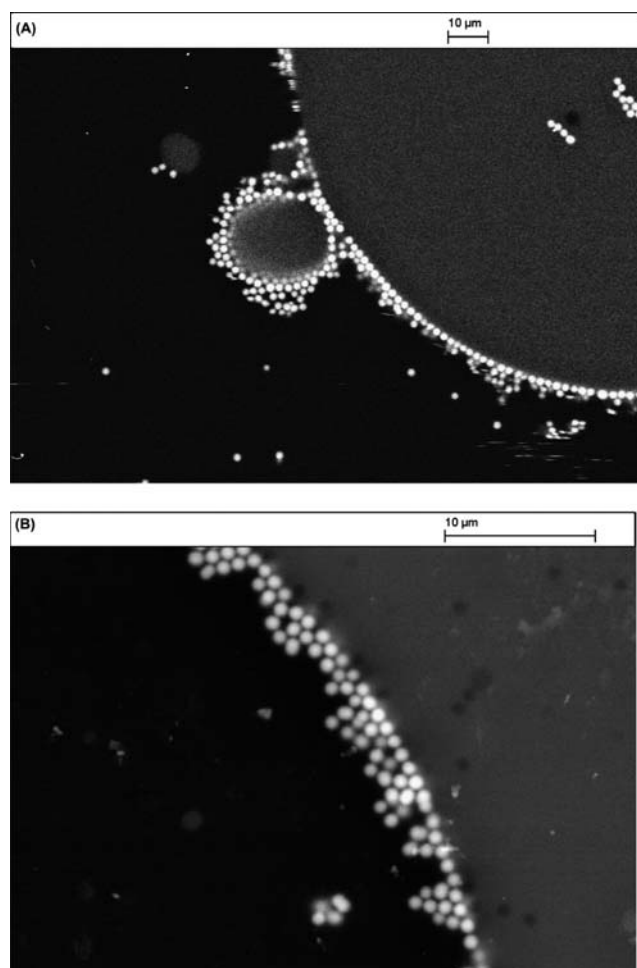


Fig. 3 SEM images for emulsions stabilised by different types of solid particles. (A) A water-in-tricaprylin (w/o) emulsion stabilised by 1 wt% of 2.2 μm hydrophobic silica particles. Water drops are in grey and the oil continuous phase is the black area. (B) tricaprylin-in-water (o/w) emulsions stabilised by 1.1 μm aliphatic amine PS latex particles.

shown in a planar oil–water interface.¹⁰ A close-packed particle monolayer was seen around the edge of the oil droplet as revealed from the higher magnification image (see ESI†). We were able to observe and confirm the other emulsion type (w/o) by dispersing the more hydrophobic silica particles into the oil phase. Fig. 3a shows SEM image of water-in-tricaprylin emulsion ($\phi_w = 0.17$) stabilised by 2.2 μm silica particles. The particle monolayer can be clearly seen around the water droplets and most of the silica particles are preferentially protruded into the continuous oil phase, indicative of their

hydrophobicity (more images in ESI†). We found that a particle bilayer is formed between the two adjacent water droplets, which has been considered one of the stabilisation mechanisms of solid-stabilised emulsions.¹⁰ An interesting observation occurred when the SEM magnification was higher, where the adsorbed particle monolayer adsorbs and desorbs in a random way but forms one monolayer between these two processes. We have recorded a unique video using SEM showing this phenomenon for the first time *in situ* for a solid-stabilised emulsion system (see ESI†).

Fig. 3b presents a SEM image for a big oil droplet (black area) stabilised by 1.1 μm PS latex particles initially dispersed in water containing 1.6 wt% NaCl to allow them to attach to the oil–water interface. We noticed the presence of some dark voids in the water continuous phase having similar sizes to the latex particles, indicating that they might have been moved to the oil–water interface.

In summary, we have studied the interfacial structure of solid-stabilised emulsions using the WETSEM technique for the first time. Our method allows the clear observation of live water or oil emulsion droplets stabilised by solid particles. Emulsion type and particle locations were also determined. We were able to clearly see solid particles at the curved interface having diameters > 500 nm. An interesting extension of this technique would be to study in detail the effect of particle hydrophobicity on the contact angle θ they form at the oil–water interface and correlate that with the stabilisation mechanism of solid-stabilised emulsions, which is still largely unresolved. This would open up an exciting way to study those technologically important systems that involve adsorption and interaction of solid particles at liquid–liquid or air–liquid interfaces. Such a study is under way.

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