



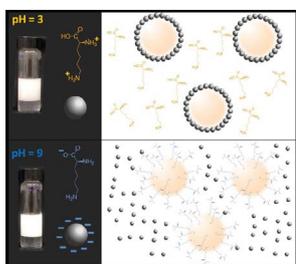
## Multi-modal stabilisation of emulsions using a combination of hydrophilic particles and an amino acid



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### GRAPHICAL ABSTRACT



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### ABSTRACT

Emulsions have been formed using non-traditional particle stabilisers: hydrophilic silica particles which themselves are stabilised in suspension by L-lysine. The particles are produced using an adapted recipe for the production of monodisperse nanoparticles (NPs) of small size (15 nm), with L-lysine used as a stabiliser and catalyst during particle synthesis – and are termed SiO<sub>2</sub>@Lysine. The resultant SiO<sub>2</sub>@Lysine suspensions (particles and residual L-lysine) are used to study the pH-dependent stabilisation of hexadecane-in-water emulsions. Our results show that it is possible to stabilise hexadecane-in-water emulsions using these 15 nm SiO<sub>2</sub>@Lysine NPs when the pH of the system is fixed either at acidic pH (e.g. pH = 2.5) or alkaline pH (e.g. pH = 9.0). At high pH, the experimental evidence indicates that L-lysine acts as the primary stabiliser. In contrast, at low pH, silica nanoparticles can stabilise an oil-in-water emulsion, apparently without the aid of the free L-lysine molecules. This multi-modal action of the silica/amino acid suspension has produced an emulsion that is stable at extreme pH values and unstable at intermediate pH values, and one that is a Pickering emulsion at low pH and a traditional emulsion at high pH. Such divergent properties and behaviour may be of relevance for food or pharmaceutical applications.

### 1. Introduction

Many types of inorganic and organic colloidal particles have been used to stabilise emulsion droplets [1–3]. Colloidal silica (SiO<sub>2</sub>) particles are often used, as they can be easily prepared with variable size and surface functionalisation [4–9]. In addition, they are chemically inert, mechanically stable, and most importantly they are biocompatible [10]. Most studies have been performed with hydrophobic (surface-modified)

SiO<sub>2</sub>, as their application as particle stabilisers is known to be optimal when their contact angle approaches 90°. Much of our knowledge of the efficacy of SiO<sub>2</sub> as a particle stabiliser comes from the Binks group, who performed many systematic studies with SiO<sub>2</sub>, including the influence of their wettability on the type and stability of water-toluene emulsions [11,12].

In addition to the issue of hydrophobicity, another aspect that influences the use of SiO<sub>2</sub> particles as emulsion stabilisers is the need to

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account for (or mitigate against the influence of) the charge at the interface of the SiO<sub>2</sub> (negative, and of significant magnitude at most pH values). The oil droplets in an emulsion are usually negatively charged, and the resultant electrostatic repulsion with negatively charged particles may strongly hinder particle adsorption, due to the existence of an adsorption barrier [13]. As a result, significant drop–drop coalescence, followed by phase separation, may occur during and after emulsification, even at high particle concentrations.

The use of chemically-bonded surface modifiers on silica particles is perhaps the most common means to overcome both the barriers of hydrophilicity and surface charge. A different approach involves the use of surfactants in combination with hydrophilic silica particles. It is well known that surfactants decrease the oil/water (o/w) interfacial tension ( $\gamma_{ow}$ ) and consequently, the energy of adsorption of particles to the interface will decrease proportionally [14–17]. It has also been proven that surfactants may modify the wettability of the particles and promote their adsorption at the oil/water interface [18,19]. The synergy between particle and surfactant mixtures has been exploited to make particle-stabilised emulsions [20–22]. Different types of surfactants can be used: ionic, non-ionic, short amphiphilic and even zwitterionic [23–25]. Furthermore, many commercial emulsion formulations contain mixtures of surfactant, amino acids or proteins and particles, it is of interest to study the mechanisms of the emulsions stabilised by such mixtures [15,26–30].

The focus of this work is the use of L-lysine as the surfactant in combination with hydrophilic silica particles as emulsion stabilisers. Both components are biocompatible so the generated emulsions may be of interest for the pharmaceutical industry. There exists some prior work on the interaction of lysine with silica particles. As reported by Kitadai, Yokoi and later by Bharti, L-lysine does adsorb on the surface of SiO<sub>2</sub> particles at pH around 9.7 [5,6,31,32].

Another feature of our current work is the focus on small silica particle size. Due to the difficulty in the preparation of hydrophilic SiO<sub>2</sub> particles via the Stöber method with sizes below 100 nm in diameter, the trend is to conduct systematic studies with SiO<sub>2</sub> particles that are quite large in size. Here we present a study in which the stability of the Pickering emulsion is evaluated using hydrophilic SiO<sub>2</sub> NPs of sizes 15 nm in diameter. This specific particle type exemplifies the three properties which are well known to be most problematic for particle stabilised emulsions: the particles are highly hydrophilic, their surface charge is significant and they are smaller than 100 nm.

Hence in this work, the stabilisation of oil-in-water emulsions using 15 nm L-lysine stabilised silica particles (termed SiO<sub>2</sub>@Lysine NPs hereafter) is investigated, particularly focusing on the synergistic effect of having both L-lysine and silica present in the system. The adsorption of L-lysine onto the silica surface is pH dependant, leading up to the investigation of the stability of the emulsions at different pH values: at high pH, where the SiO<sub>2</sub> is known to be charged due to the deprotonation of the silanol groups (and L-lysine adsorbs at the SiO<sub>2</sub> surface); and at low pH, close to the isoelectric point of the SiO<sub>2</sub> NPs [33–35] (where L-lysine will be desorbed from the SiO<sub>2</sub> surface).

## 2. Materials and methods

### 2.1. Materials

Tetraethyl orthosilicate (TEOS ReagentPlus<sup>®</sup>, ≥99% product No. 236209) was purchased from Aldrich. L-lysine (98%, TLC product No. L5501) and hexadecane (≥99%, product No. H0255) were obtained from Sigma. All chemicals were used without further purification with the exemption of hexadecane. Before use, hexadecane was passed 3 times through basic alumina (99%, Acros Organics) to remove polar impurities and several cycles of washing with Fluorosil<sup>®</sup> were carried out. The purification of the hexadecane proceeded until the measured interfacial tension for oil/water was independent of time and had a value of 53.3 mN m<sup>-1</sup>. The water in all experiments was prepared in a

three-stage Millipore Milli-Q Plus 185 purification system and had a resistivity higher than 18.2 MΩ cm, surface tension 72.8 mN m<sup>-1</sup>, specific conductivity < 0.5 μS cm<sup>-1</sup> and pH ≈ 5.5 at 25 °C.

### 2.2. Nanoparticle synthesis

The SiO<sub>2</sub> NPs were synthesised according to the original method reported by Wang et al. [6], with slight modifications. To synthesise SiO<sub>2</sub> NPs sizes of 15 nm, typically, 7.72 mL of TEOS (0.25 mol) was added to 92.3 mL of the aqueous solution of L-lysine (6.2 mM) at 60 °C under stirred conditions, using a magnetic stirrer at 500 rpm with a Teflon-coated stirring bar (15 × 7 mm<sup>2</sup>). The mixture underwent further stirring for 48 h. The reaction system was initially bi-phasic due to the poor solubility of TEOS in water and gradually turned into a homogeneous dispersion during the reaction time under stirring, yielding 15 nm SiO<sub>2</sub> particles with the surfaces coated with L-lysine, referred to as SiO<sub>2</sub>@Lysine nanoparticles (SiO<sub>2</sub>@Lysine NPs).

### 2.3. Nanoparticle characterisation

Transmission electronic microscopy (TEM) imaging of the synthesised NPs was performed on an FEI Tecnai G2 Spirit Transmission Electronic Microscope operating at an acceleration voltage of 120 kV, equipped with a FEG LaB6 emitter and BioTWIN lens design. Imaging was done via an in-column Olympus-SIS Veleta CCD camera. Five microlitre droplets of each sample were dropped onto a piece of ultrathin Formvar-coated 200-mesh copper grid (GSCu200CH-100 ProSciTech) and left to dry in air. In order to determine the diameter, as well as the diameter distribution of the resulting NPs based on their TEM images, at least 100 NPs were measured with the aid of the graphics editing program ImageJ<sup>®</sup> [36]. These results were compared to the diameter and diameter distribution obtained by dynamic light scattering (DLS).

DLS was used to study the synthesised particles using a Malvern Zetasizer Nano ZS, UK, which has a size detection range of 0.3 nm to 10 μm. The experiments were performed at room temperature and at a fixed angle of 173° using a 50 mW, 633 nm laser and a digital auto-correlator. Water (refractive index,  $n = 1.33$ ) was used as the dispersant in the DLS analysis. Size distribution results are expressed as the z-average diameter (i.e. the intensity-weighted mean hydrodynamic diameter) together with the polydispersity index (PDI) indicating the width of the size distribution. The number-average values were used to compare the sizes and size distributions of the SiO<sub>2</sub> NPs as the number-average hydrodynamic sizes were more comparable to the particle sizes obtained from TEM images.

Zeta potential,  $\zeta$ , of the synthesised particles was determined by phase analysis light scattering (PALS) technique (Malvern Zetasizer Nano ZS, UK) at 25 °C. The mean zeta potential was computed based on the electrophoretic mobility (i.e. the ratio of the velocity of particles to the field strength) by applying the Smoluchowski theory. For that measurement, 600 μL of the sample were placed in a disposable cuvette. To evaluate the influence of the pH on  $\zeta$  values of the SiO<sub>2</sub> NPs, prior to the measurements of the electrokinetic mobility of the particles, the SiO<sub>2</sub> dispersions were adjusted at different pH from low to high pH with volumes of NaOH (1 and 0.1 M) and HCl (1 and 0.1 M) added dropwise, using a 100 μL micropipette. The pH was measured after a short time with a glass pH electrode which was previously calibrated using standard aqueous buffer solutions.

### 2.4. Interfacial characterisation

Measurements of the interfacial tension ( $\gamma$ ) were performed with a Profile Analysis Tensiometer PAT1 M (Sinterface, Germany) employing the emerging bubble (for air/water systems) geometry. The cleaning procedure of the cuvette involved soaking in 1–2 M KOH (15 min), followed by rinsing with Milli-Q water, drying with N<sub>2</sub> and exposure to air plasma for 60–90 s. The cuvette was used immediately for the

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