



Research paper

Synergistic stabilization of Pickering emulsions by in situ modification of kaolinite with non ionic surfactant



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ABSTRACT

Synergistic stabilization of decane/water emulsions with a combination of kaolinite and non ionic surfactant SPAN-80 is explored. Pure kaolinite being charged and very hydrophilic is a poor stabilizer of emulsions even when sufficient quantity of salt is added to screen electrical double layer interactions. However, the hydrophobicity (via. contact angle) of kaolinite can be tuned with increasing concentration of SPAN-80 leading to very stable O/W emulsions when both kaolinite and SPAN-80 are used. This is due to increase in hydrophobicity of kaolinite particles due to surfactant adsorption which enables them to get adsorbed at oil/water interface more efficiently. Adsorption of kaolinite at emulsion droplets is demonstrated through fluorescently labeled kaolinite. Emulsions phase inverted from O/W to W/O at very high concentrations of surfactant. This phase inversion is due to competitive adsorption of excess unadsorbed surfactant. Other general features such as the effect of salt, pH, oil/water ratio on emulsion formation, stability, type and droplet size has been studied.

1. Introduction

Particle stabilized emulsions and foams have gained attention in recent years owing to their high stability and versatility of their application in several fields. They were first discovered by Sir Spencer Pickering (Pickering, 1907) and Ramsden (Ramsden, 1903). Pickering emulsions owe their stability to a thin, elastic layer of adsorbed particles at droplet interface. Particle layer prevents the droplet coalescence and imparts long term kinetic stability to these emulsions. Pickering emulsions have been made with a large variety of nanoparticles ranging from metal organic frameworks (MOFs) (Sabouni and Gomaa, 2015), metal oxides (Bachinger and Kickelbick, 2010), silica (Frelichowska et al., 2009), polystyrene (Golemanov et al., 2006) and natural materials such as whey protein (Destribats et al., 2014), cellulose nano crystals (Kalashnikova et al., 2011), chitosan (Wei et al., 2012), Zein (de Folter et al., 2012) and numerous other materials.

Hydrophobicity and charge of particle play a major role in determining the formation as well as type of emulsion. Particles which are super hydrophilic ($\theta \ll 90^\circ$) or super hydrophobic ($\theta \gg 90^\circ$) cannot stabilize emulsions due to their poor adsorption at oil/water interface. However, when contact angle of particle is such that the particles are partially wettable by either of the fluids (generally $50^\circ < \theta < 130^\circ$), particles participate in emulsification and form very stable emulsions. Partially hydrophilic particles tend to stabilize O/W emulsions while partially hydrophobic particles tend to stabilize W/O emulsions. This

empirical rule is called Bankroft rule (Golemanov et al., 2006). Similarly particles which are highly charged experience repulsion from the oil/water interface due to image charge effect (Wang et al., 2012) and are very poor stabilizers of emulsions. In practice, a small amount of electrolyte/pH adjustment (Yang et al., 2007)/oppositely charged particles (Nallamilli et al., 2015) are added thus enabling them to stabilize emulsions.

In general, most of the widely used materials including silica, metal oxides, protein nanoparticles etc. are either highly hydrophilic or highly hydrophobic. In recent years several techniques have been devised to tune the contact angle of particle in order to enable them stabilize emulsions. These techniques can be broadly put into two categories (a) methods where particles are pretreated chemically with suitable chemicals (Binks and Murakami, 2006) (e.g. silanes/chlorosilane/fluorosilane) thus rendering them with desired contact angle and (b) methods where additional components (amphiphiles/surfactants) are added to emulsions along with particles which modify the contact angle of particles in situ, this is referred to as “synergistic stabilization”. Both methods are of interest as tuning particle properties provides good control over type of emulsion formed and emulsion phase inversion. A wide variety of amphiphilic molecules can be used to achieve synergistic stabilization. To mention a few, Binks et al. (2007) used hydrophilic silica particles and cationic/anionic surfactant to stabilize *n*-dodecane/water emulsions. Cui et al. (2011) used calcium carbonate nanoparticles with fatty acids and achieved multiple phase

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inversion in emulsions so stabilized. Dong et al. (2014) modified Montmorillonite with bis(2-hydroxyethyl)oleylamine and stabilized seawater-in-oil emulsions. Phase inversions occurred by altering surfactant to kaolinite ratio and oil to water ratio. Worthen et al. (2014) used hydrophilic silica nanoparticles and zwitterionic surfactant, caprylamidopropyl betaine (CPAB) to achieve synergistic stabilization of synthetic seawater/dodecane emulsions.

In particular, synergism between natural kaolinite and surfactants in stabilizing Pickering emulsion systems has been widely explored in recent years. Owing to wide availability, low cost, high surface area per unit mass and versatile applicability of kaolinite in various industries, this combination has received high attention in Pickering emulsion community. A particularly interesting feature of kaolinite/surfactant combination is possibility of having single or multiple phase inversions. Lagaly et al. (1999a,b) used smectite kaolinites along with non ionic surfactants to stabilize paraffin/water emulsions. Zhang et al. (2013) also reported phase inversions in emulsions stabilized by Laponite kaolinite and non ionic surfactant SPAN-80. Zhang et al. (2014) reported double inversions with Montmorillonite and CTAB combination. Wang et al. (2008) reported double phase inversions in emulsions stabilized by layered double hydroxides and sodium-dodecyl sulphate. Wang et al. (2010) stabilized emulsions synergistically by poly(oxypropylene)diamine and laponite kaolinite particles. Rege et al. (2011) used Laponite and hydrophobin (a fungi derived protein) synergistically to stabilize emulsions.

Although use of mixture of kaolinite-surfactant system for emulsion stabilization is reported, most of the studies use other clay minerals such as Montmorillonite, Bentonite, Hectorite, Palygorskite, etc. Detailed emulsification studies using Kaolinite are comparatively few (Gu et al., 2003; Jiang et al., 2010; Wang and Alvarado, 2011). Kaolinite plays a major role during extraction of crude oil forming water/oil emulsions thus there is huge interest in understanding behavior of kaolinite stabilized emulsions. Synergistic effect of non ionic surfactant SPAN-80 on kaolinite in stabilizing decane-water emulsions is discussed. System phase inverts from O/W to W/O as surfactant concentration was increased at fixed kaolinite concentration. Increase in surfactant concentration changes the kaolinite form being hydrophilic to partially hydrophobic, which is confirmed through contact angle measurements. Based on these observations it is hypothesized that, at low surfactant concentrations, surfactant modified kaolinite dominates the emulsion type. In contrast, at high surfactant concentrations, surfactant adsorption on kaolinite saturates and the excess surfactant competes with kaolinite and dominates the emulsion type leading to phase inversion. Other aspects of emulsification such as droplet size variation with pH, effect of salt, phase inversion due to change in oil/water ratio etc. were also studied. Adsorption of kaolinite particles to droplet surface was also demonstrated by observing emulsion droplets stabilized by fluorescently labeled kaolinite particles.

2. Materials & methods

2.1. Materials

Kaolinite was purchased from Alfa Aesar (USA). Kaolinite was in form of white powder with density of 2.25 g/cm³. Figure S11 (Supporting information) shows HR-SEM image of kaolinite particles which are typically in form of stacked up hexagonal layers of size approximately 200 nm–3 μm and thickness < 50 nm. SPAN-80 (sorbitan monooleate) was purchased from Loba Chemie (Mumbai, India). SPAN-80 is an oil soluble surfactant with a hydrophilic-lipophilic balance (HLB) value of 4.3 and is poorly soluble in water. It is widely used surfactant in food industry. Rhodamine 6G was purchased from Sigma Aldrich (Bengaluru, India.). *n*-Decane (purity > 99% AR grade) was purchased from Alfa Aesar (USA). Decane was treated with alumina to remove polar impurities. Deionized water from a Milli-Q system (Millipore) was used for all experiments. Its resistivity was > 18.2 MΩ-

cm.

3. Methods

3.1. Determination of zeta potential of kaolinite in water

Aqueous kaolinite dispersions were prepared at 0.05 wt% and the electrolyte concentration was adjusted to values ranging from 10 mM (Debye length, $\kappa^{-1} = 3$ nm) to 2 M of NaCl for zeta potential measurements. Horiba particle size analyser (model SZ-100) was used for these measurements. About 150 μL of sample was loaded in electro-phoretic cell with built in electrodes for measurements. Since typical particle size of kaolinite was about 200 nm to 3 μm, we use thin double layer approximation (i.e. Smoluchowski model) to estimate electro-phoretic mobility and thus zeta potential values.

3.2. Preparation of kaolinite pellets and contact angle measurements

Compressed disk method (Yan and Masliyah, 1996) was used to determine contact angles. Kaolinite tablets were prepared by compressing kaolinite powder into a cylindrical tablet form in a manually operated pellet press under a maximum pressure of 6 ton-force/in². The diameter of the tablets was 13 mm and thickness was about 3 mm. Contact angles were measured using a goniometer (GBX Digidrop) with automated image analysis software. Kaolinite tablets were placed inside a plastic cuvette (1 cm × 1 cm × 2 cm) with clear faces on four sides (typically used in particle size analyser) and decane containing various concentrations of SPAN-80 was gently poured in the cuvette over the kaolinite tablet. A water droplet of about 1–1.5 μL volume was placed on the kaolinite pellet under decane using a calibrated syringe and images were captured and analyzed to obtain the contact angles of the water drop on a kaolinite tablet submerged in decane containing different concentration of SPAN-80.

3.3. Preparation of kaolinite-SPAN 80 dispersions

To study the dispersion behavior of kaolinite particles in decane, kaolinite dispersions were prepared by mixing 0.1 g of kaolinite in 4 mL of decane phase containing different concentrations of SPAN-80. Contents of the vials were mixed vigorously for 5 min in a vortex mixer. The contents of the vials were observed over time for analysis of stability of kaolinite particles in decane.

3.4. Preparation of emulsions

Emulsions were prepared by mixing water phase containing desired concentration of kaolinite particles and decane phase containing desired concentration of surfactant and emulsifying the contents using a lab homogenizer (Ultra Turrax) at constant speed of 13,000 rpm. Smaller volume samples (used for determining emulsion type) were prepared using a vortex mixer at 2500 rpm. These emulsions were later used for stability and drop size estimation. To prepare fluorescent emulsions, Rhodamine 6G was first dissolved in water at concentration of 10⁻⁵ M. 1 g of kaolinite was dispersed in 30 mL of dye solution, vigorously dispersed in a vortex mixer and kept undisturbed for one hour. The kaolinite particles were centrifuged at 12,000 rpm. Supernatant containing unadsorbed dye was discarded and kaolinite particles were washed with distilled water for 3 times and finally recovered and used for emulsion preparation. Peak excitation wavelength of Rhodamine 6G is 526 nm and Peak emission wavelength is 555 nm.

3.5. Drop size and emulsion type determination

Drop test was used to determine the type of emulsion. An inverted microscope (Leica 3000B) equipped with 10×, 20× and 63× objectives was used to acquire images of emulsion droplets. Microscopy

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