Journal of Colloid and Interface Science 463 (2016) 288–298

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Interfacial adsorption and surfactant release characteristics of magnetically functionalized halloysite nanotubes for responsive emulsions

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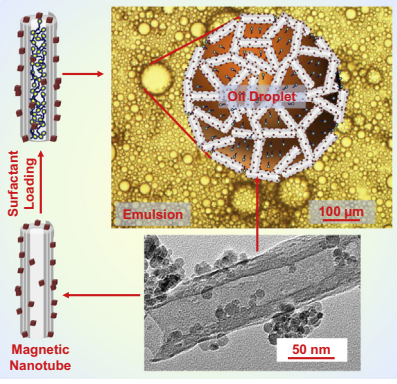
GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 August 2015
Revised 25 October 2015
Accepted 27 October 2015
Available online 30 October 2015

Keywords:
Emulsion
Iron oxide
Halloysite nanotubes
Magnetic responsiveness
Surfactant
Encapsulation

ABSTRACT

Magnetically responsive oil-in-water emulsions are effectively stabilized by a halloysite nanotube supported superparamagnetic iron oxide nanoparticle system. The attachment of the magnetically functionalized halloysite nanotubes at the oil–water interface imparts magnetic responsiveness to the emulsion and provides a steric barrier to droplet coalescence leading to emulsions that are stabilized for extended periods. Interfacial structure characterization by cryogenic scanning electron microscopy reveals that the nanotubes attach at the oil–water interface in a side on-orientation. The tubular structure of the nanotubes is exploited for the encapsulation and release of surfactant species that are typical of oil spill dispersants such as dioctyl sulfosuccinate sodium salt and polyoxyethylene (20) sorbitan monooleate. The magnetically responsive halloysite nanotubes anchor to the oil–water interface stabilizing the interface and releasing the surfactants resulting in reduction in the oil–water interfacial tension. The synergistic adsorption of the nanotubes and the released surfactants at the oil–water interface results in oil emulsification into very small droplets (less than 20 μm). The synergy of the unique nanotubular morphology

Abbreviations: HNT, halloysite nanotubes; M-HNT, magnetically functionalized halloysite nanotubes; Tween 80, polyoxyethylene (20) sorbitan monooleate; Span 80, sorbitan monooleate.

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http://dx.doi.org/10.1016/j.jcis.2015.10.064

Release
Interfacial tension

and interfacial activity of halloysite with the magnetic properties of iron oxide nanoparticles has potential applications in oil spill dispersion, magnetic mobilization and detection using magnetic fields.

1. Introduction

The adsorption of solid particles at the oil–water interface is useful in variety of applications including materials synthesis, interfacial catalysis and emulsion stabilization [1,2]. The magnetic functionality of iron oxide nanoparticles have stimulated their application in the preparation of magnetically responsive emulsions, oil mobilization and remote detection of the oil–water interface [3–5]. In particle stabilized emulsions, the partial wetting of particles by both the oil and aqueous phases drives the partitioning of the particles to the oil–water interface [6,7]. The underlying concept behind the stabilization of emulsions by particles is the fact that the particles are held at the oil–water interface with energies that are several orders of magnitude higher than the thermal energy thereby providing a large steric hindrance to droplet coalescence [1,6,8,9].

Free energy analysis on a particle at a planar oil–water interface gives the work required to desorb the particle from the interface into a bulk phase in terms of the free energy change (ΔG) [1]. For instance, the free energy change (ΔG) on removing a cylindrical particle from the interface into the bulk aqueous phase can be expressed as [10]:

$$\Delta G = 2rL\gamma_{ow}\left[\sin\theta - \theta\cos\theta\left(1+\frac{r}{L}\right) + \frac{r\cos^2\theta\sin\theta}{L}\right] \quad (1)$$

where γ_{ow} is the oil–water interfacial tension, r is the radius of the cylindrical particle, L is the particle length and θ is the contact angle [10]. Using Eq. (1), the work required to detach a 1 μm long cylindrical particle with a radius of 50 nm at a 30° contact angle and interfacial tension of 49 mN/m is calculated to be 5.54×10^4 kT.

Similar analysis for the detachment of a spherical particle into the aqueous phase gives [1]:

$$\Delta G = \pi r_s^2\gamma_{ow}(1-\cos\theta)^2 \quad (2)$$

where γ_{ow} is the oil–water interfacial tension, r_s is the radius of the spherical particle, and θ is the contact angle [1]. From Eq. (2), the work required to detach a spherical particle of the same volume as the cylindrical particle above (r_s = 123.3 nm) at a 30° contact angle and interfacial tension of 49 mN/m is calculated to be 1.12×10^4 kT.

The high energy of attachment at the oil–water interface makes particulate emulsifiers effective in preventing droplet coalescence. However, the adsorption of the particles at the interface does not reduce interfacial tensions sufficiently for optimal emulsification [11,12]. The lowering of the oil–water interfacial tension can be achieved by the combination of particle and surfactant emulsifiers [13–15]. Pichot et al. investigated the synergistic mechanisms of emulsion stabilization by hydrophilic silica particles added to the aqueous phase and monoolein surfactant added to the oil phase [16]. The monoolein surfactant was reported to play key roles of lowering the interfacial tension, inducing droplet break-up during emulsification and delaying droplet coalescence until the silica particles assemble at the oil/water interface [16].

The methods employed in treating oil spills include physical containment with booms, mechanical recovery with skimmers, chemical herding, in-situ burning, dispersion and biodegradation [17]. In calm ocean conditions and in arctic conditions in the presence of ice floes, chemical herding can be used to thicken oil slicks to for easy recovery or in-situ burning without the need for mechanical containment [18]. In the dispersion of oil spills into the water column, surfactant solutions are typically applied to lower the oil–water interfacial tension and break up oil spills into droplets with minimal wave energy, thereby providing a large oil–water interfacial area for biodegradation [19,20]. The energy required to create droplets and thereby increase interfacial area can be expressed as:

$$\Delta G = \gamma_{ow} * \Delta A \quad (3)$$

the product of the oil–water interfacial tension (γ_{ow}) and interfacial area (ΔA) [1]. Dispersant formulations contain a significant amount of solvents such as propylene glycol and there is considerable interest in reducing solvent levels and effectively delivering surfactant components [21].

We recently exploited the unique nanotubular morphology of halloysite nanotubes (HNT) for the loading and release of surfactant from the pore volume of the tubes, lowering the crude oil–saline water interfacial tension to values of 10^{-2} mN/m [10]. The nanotubes attach to the oil–water interface, thereby allowing a release of surfactant to the oil–water interface and dispersion of oil into small droplets. Here, we functionalize the HNT surface with superparamagnetic iron oxide nanoparticles for the preparation of magnetically responsive oil-in-water emulsions. We characterize the release of surfactant from the magnetically-functionalized halloysite nanotubes (M-HNT), synergistic particle–surfactant stabilization of emulsions over extended time periods and the structure of the oil–water interface. The integration of superparamagnetic nanoparticles within the hollow scroll-like nanostructure of halloysite (HNT) and the interfacial activity of the resulting magnetic nanotubes may find potential applications in oil spill dispersion, interfacial release of spill treating agents, magnetic mobilization and as magnetic contrast agents for enhanced oil spill detection [22,23].

2. Experimental

2.1. Materials

Iron(III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), dioctyl sulfosuccinate sodium salt (DOSS, 98%), polyoxyethylene (20) sorbitan monooleate (Tween 80), sorbitan monooleate (Span 80), methanol and dodecane were purchased from Sigma–Aldrich. Iron(II) sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$, ⩾99.0%), sodium chloride (NaCl, certified ACS grade) and ammonium hydroxide solution (ACS reagent, 28.0–30.0% NH_3 basis) were obtained from Fisher Scientific. Halloysite nanotubes (HNT) were obtained from NaturalNano. Inc. (Rochester, NY, USA). The characteristic dimensions of the HNT range from about 0.33–1.5 μm in length, 90–250 nm in external diameter and 10–70 nm in lumen. All materials were used as received. Deionized (DI) water, produced from an Elga water purification system (Medica DV25), with resistivity of 18.2 MΩ cm was used in all experiments. 0.6 M sodium chloride solution in deionized water was used as a substitute for seawater.