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Regular Article

Manipulation of Pickering emulsion rheology using hydrophilically modified silica nanoparticles in brine

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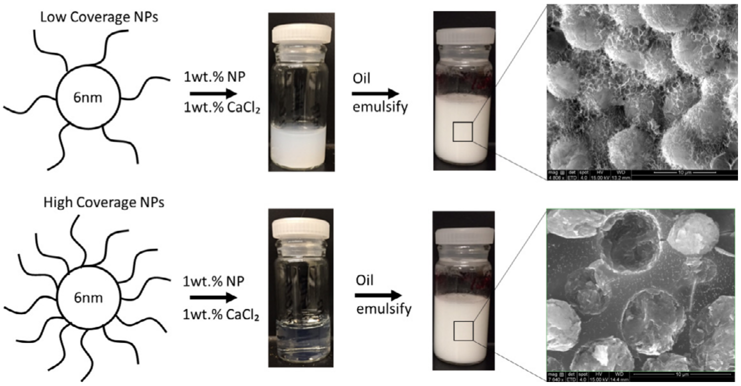
GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Previous work on Pickering emulsions has shown that bromohexadecane-in-water emulsions (50% oil) stabilized with fumed and spherical particles modified with hexadecyl groups develop a noticeable zero shear elastic storage modulus (G'_0) of 200 Pa and 9 Pa, respectively, while in just 50 mM NaCl. This high G'_0 can be problematic for subsurface applications where brine salinities are higher and on the order of 600 mM NaCl. High reservoir salinity coupled with low formation pressure drops could prevent an emulsion with a high G'_0 from propagating deep into formation. It is hypothesized that G'_0 of an emulsion can be minimized by using sterically stabilized silica nanoparticles modified with the hydrophilic silane (3-glycidyloxypropyl)trimethoxysilane (glymo).
Experiments: Bromohexadecane-in-water emulsions were stabilized with low and high coverage glymo nanoparticles. Oscillatory rheology was used to monitor G'_0 as a function of nanoparticle concentration, oil volume fraction, salinity, and pH. Cryogenic scanning electron microscopy was used to make observations on the emulsion microstructure.
Findings: G'_0 of bromohexadecane-in-water emulsions were minimized by using particles with a high coverage of glymo on the particle surface, which reduced the Ca^{2+}/silanol site interactions. Emulsions that were stabilized with low surface coverage particles had noticeably higher G'_0, however, their G'_0 could be reduced by a factor of 3.3 by simply lowering the solution pH to 3. Cryo-SEM images showed that nanoparticle bridging was more pronounced with nanoparticles that had low glymo coverage as opposed to high coverage.

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1. Introduction

Pickering emulsions are emulsions stabilized with solid amphiphilic particles as opposed to chemical surfactants [1] and are kinetically stable to coalescence due to the irreversible adsorption of solid particles to the interface between two immiscible fluids [2]. The appropriate selection of a nanoparticle surface modifier plays an integral role in how well particles are dispersed in a particular system [3,4] and is one of the key parameters that influence the stability and rheological properties of a solid particle-stabilized (Pickering) emulsion [5].

For aqueous systems consisting of particles dispersed in pure water, two effective routes for altering the wettability of silica particles and controlling the type of emulsion that is formed (oil-in-water vs. water-in-oil) are modifying the surface by covalent attachment of hydrophobic alkoxysilanes and adsorbing surfactants by electrostatic interactions [6]. For example, Binks and Lumsdon [7]characterized emulsions stabilized with partially hydrophilic silica particles (76% silanol coverage) by reacting the particles with dimethyldichlorosilane and found they were capable of stabilizing toluene-in-deionized water emulsions, and conversely, those with intermediate wettabilites (50–67% silanol coverage) or hydrophobic (20% silanol coverage) could stabilized deionized water-in-toluene emulsions.

Adding salts to the aqueous phase of an oil-water system (containing nanoparticles) complicates the fate and destination of particles at the fluid interface. Whitby et al. [8] illustrated this with bromohexadecane-in-water emulsions (1:1) stabilized with partially hydrophilic fumed silica particles that were modified with hexadecyl chains. These dilute emulsions, which were well below the random close packing of hard spheres (φ = 0.635), developed a yield stress of 1 Pa in the presence of just 1 mM NaCl which further increased to 10 Pa in 400 mM NaCl. The positively charged sodium ions interacted with deprotonated particle silanol sites [9]. This process imparted hydrophobicity and reduced the particle electrical double layer, which promoted particle flocculation and their arrangement into a dense monolayer at the interface between droplets of oil and water. In addition, because the particle concentrations were high ($\sim$2 wt%) and the anchored hexadecyl groups were poorly solvated in brine [10], an aggregated network of particles formed in the continuous phase. This network was responsible for the yielding behavior of the emulsions and provided additional emulsion stability by retarding creaming/coalescence [9]. These properties have been observed elsewhere with emulsions stabilized with clay [11], silica [9,12], alumina [13], and layered double hydroxide particles [14].

For subsurface applications, where the salinity of brines is comparable to seawater (0.6 M NaCl) and can be as high as 22% total dissolved solids [15], silica particles modified with hydrophobic alkoxysilanes are a poor choice as foam or emulsion stabilizers for enhanced oil recovery. This is because the formation of a percolating network of particles can be detrimental in propagating an emulsion deep into a formation, where pressure drops are low and on the order of several to ten psi/ft [16]. In addition, if the foam or emulsion were to de-stabilize, the hydrophobically modified particles would precipitate out of solution and potentially block pore throats, which could reduce reservoir permeability [17]. Therefore, there is a need to explore particles modified with hydrophilic silanes that are stable against aggregation in concentrated brine waters [15], but also capable of adsorbing to the oil/water interface such that foams or emulsions can be stabilized.

At present, Pickering emulsion research has focused on using silica particles to stabilize emulsions with low concentrations of mono- (<400 mM NaCl) and divalent (<10 mM) ions in solution with the intent of improving emulsion stability [9,12,18–21]. Significantly less attention has been given to emulsions stabilized with sterically stabilized hydrophilic particles in concentrated brines. In the limited studies that do explore these conditions, the information on the structure and the amount of surface modifier is minimal [22] and the rheological properties of the generated emulsions are often neglected [23,24].

Therefore, in this work, we stabilized oil-in-water (o/w) emulsions with 6 nm silica nanoparticles modified with low and high concentrations of hydrophilic, ring-opened (3-glycidyloxypropyl) trimethoxysilane (glymo). The selection of glymo as a surface modifier was due to its stability in American Petroleum Institute (API) brine (8 wt% NaCl, 2 wt% $CaCl_2$) for up to 30 days at 80 °C [15]. In addition, glymo-modified silica nanoparticles have yet to be tested as emulsifying agents and are therefore an attractive particle to evaluate for subsurface applications. We characterized the emulsion properties by monitoring their elastic storage moduli as a function of particle surface coverage, pH, salt concentration ($CaCl_2$), and aqueous phase nanoparticle concentration and show that emulsion rheology can be tuned primarily by augmenting the particle surface with different concentrations of glymo. In addition, we made observations of the microstructure of the emulsions using cryogenic scanning electron microscopy (cryo-SEM).

2. Experimental section

2.1. Materials

NexSil 6 nanoparticles (6 nm silica particles) were purchased from Nyacol Technologies. The stock solution contained 17 wt% nanoparticles at a pH of approximately 10. The particles have a specific surface area of 445 m^2/g (provided by the manufacturer). (3-Glycidyloxypropyl)trimethoxysilane (>98%) (glymo) and 1-bromohexadecane (97%) were purchased from Sigma-Aldrich. Calcium chloride, basic alumina, and 1 N hydrochloric acid were purchased from Fisher Scientific and used as received.

2.2. Nanoparticle functionalization

Nanoparticles were surface modified with (3-glycidyloxypropyl)trimethoxysilane (glymo) following previous work [15,25]. Glymo was added into reaction mixtures at a concentration of 1.85 or 4.00 $\mu mol/m^2$ of nanoparticle surface area for low and high surface coverage, respectively. An acid-catalyzed ring opening of the glymo epoxide was performed before adding it to the nanoparticle dispersion. This was done by reacting glymo for several minutes in DI water adjusted to pH 2 using 1 N HCl. The ring-opened glymo was added to the nanoparticle dispersion and heated overnight at 60 °C to complete the hydrolysis condensation reaction. In some cases, a small amount methanol was used to prevent glymo oligomers from precipitating out of solution, and was removed by evaporation upon completing the reaction. The final concentration of nanoparticles in the mixture was approximately 10 wt% and the final pH of the reaction mixture was 10–10.1. Batches containing 20 grams of nanoparticles were surface modified and used without purification.

2.3. Emulsion preparation

Oil-in-water (o/w) emulsions were prepared using a Branson Digital Tip Sonifier (30 W) equipped with a 5 mm microtip. Prior to generating emulsions, bromohexadecane was passed through basic alumina (2×) to remove polar impurities [8]. Bromohexadecane was selected as a model oil due to its high specific gravity (SG = 0.999), which eliminates the possibility of density driven creaming during rheological measurements [8,12]. Emulsions with