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Emulsion phase inversion from oil-in-water (1) to water-in-oil to oil-in-water (2) induced by in situ surface activation of $CaCO_3$ nanoparticles via adsorption of sodium stearate

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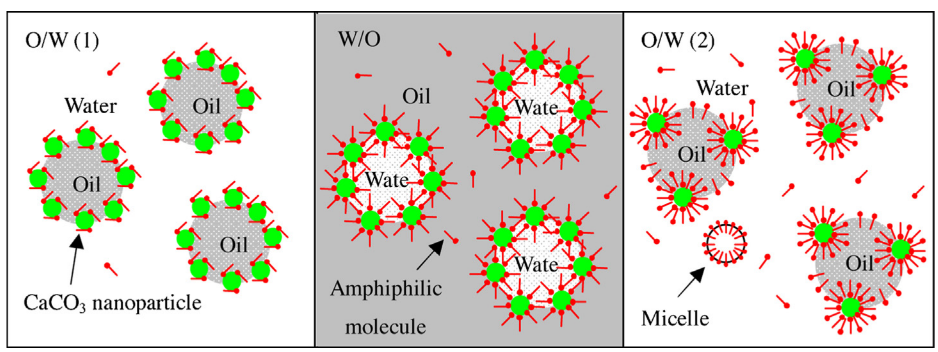
HIGHLIGHTS

- The environmentally friendly white oil–water system was used.
- Raw $CaCO_3$ nanoparticles were activated by in situ surface activation.
- A novel double phase inversion of emulsion was studied.

GRAPHICAL ABSTRACT

A double phase inversion of white oil–water emulsion, O/W (1) → W/O → O/W (2), was induced by the in situ surface activation of $CaCO_3$ nanoparticles via adsorption different amounts of amphiphilic molecules.



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ABSTRACT

In the oil exploitation process, the conversion from water-in-oil emulsion to oil-in-water emulsion is usually needed for a better cementing quality after using the water-in-oil emulsion drilling fluid. Due to the advantages of both oil-external properties for drilling and water-external characteristics for completion, the reversible emulsion drilling fluids are being used in drilling industry. The researches about phase inversion of emulsion induced by nanoparticles and amphiphilic compounds are also being conducted. Using white oil–water system, emulsion stabilized by $CaCO_3$ nanoparticles and sodium stearate was investigated. The raw $CaCO_3$ nanoparticles were activated in situ by interaction with sodium stearate in aqueous solution. The mechanism of the in situ surface activation was accessed by means of emulsion characterization, adsorption measurement and contact angle. The results show that raw $CaCO_3$ nanoparticles can be activated in situ as emulsifiers by interaction with sodium stearate. With the monolayer and bilayer formed at the $CaCO_3$ nanoparticles–water surface by absorption of different concentrations of sodium stearate, the wettability of the particles will transform from hydrophilicity to hydrophobicity and then back to hydrophilicity. The change of wettability may induce a phase inversion of emulsions from oil-in-water O/W (1) to water-in-oil W/O and re-invert to oil-in-water O/W (2). $CaCO_3$ nanoparticles can thus be used as good stabilizers of both O/W and W/O emulsions once activated in situ by mixing with suitable amounts of sodium stearate.

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1. Introduction

Oil-based drilling fluid has been used for a number of years, primarily because of their advantages such as the capability of good resistance to high temperature, strong inhibition and good lubrication when compared with water-based drilling fluid [1–4]. During the drilling process, oil-based drilling fluids can stabilize reactive shales, improve penetration rate and enhance the overall drilling efficiency. However, oil-wet borehole, drilled cuttings and filter cakes will bring great challenges in completion process [5]. Pad fluid is thus needed to be injected into the well. Ideally, the contradiction between the drilling efficiency and the well productivity can be ultimately solved in a mud process that the mud has both oil-external properties for drilling and water-external characteristics for completion [6]. A novel emulsion drilling fluid has been formulated [7]. They can be converted from W/O emulsion to O/W emulsion without undergoing a major change in rheological characteristics of the drilling fluid. W/O emulsion can improve drilling efficiency, reduce risk and stabilize the borehole. O/W emulsion can clear the well and minimize the completion damage [8].

Pickering emulsion investigated by Pickering for the first time has been applied in food, cosmetics, pharmaceutics and oil extraction industry due to their advantages such as low emulsifier usage, low toxic effects, environmentally friendly and high emulsion stability, etc. [9–14]. Many reports have described inorganic nanoparticles easily adsorb amphiphilic compound in an aqueous medium, thus changing the surface wettability [15–18]. By interaction with the amphiphilic compound, the inorganic nanoparticles can be activated in situ and become surface-active particles. The changes of wettability may induce a phase inversion, W/O → O/W or O/W → W/O, or a double phase inversion, O/W (1) → W/O → O/W (2), if the concentration of amphiphilic compound is increased to be large enough [19].

Schulman and Leja [20] found a phase inversion from water in oil emulsion (W/O) to oil in water emulsion (O/W) induced by barium sulfate particles via interaction with oleic acid. Tambe and Sharma [21] demonstrated emulsions stabilized by calcium carbonate particles would invert from O/W to W/O by increasing the concentration of stearic acid. Binks [22] used dodecane–water emulsions system and found the first example of double inversion of emulsions containing silica particles. It can invert from O/W to W/O and subsequently re-invert to O/W by increasing the concentration of surfactant didecyldimethylammonium bromide. Wang [23] described a double emulsion phase inversion induced by a mixture of SDS and layered double hydroxide (LDH) particles, in which emulsions changed from O/W (1) to W/O and subsequently back to O/W (2) upon increasing the surfactant concentration. Similar double phase inversions of emulsions induced by nanoparticles and different initial concentrations of surfactant in the aqueous phase were also reported [24–27].

As many nanoparticles are being used in drilling fluids, there exists a tentative idea that whether the double phase inversion of emulsion induced by a mixture of nanoparticles and surfactant upon increasing the surfactant concentration can be applied in drilling and completion. However, many researches about double phase inversion of emulsion induced by nanoparticles and surfactants are being conducted and many theories need to improve and perfect. Here we report a novel double phase inversion of emulsions induced by $CaCO_3$ nanoparticles and sodium stearate. $CaCO_3$ nanoparticles are the cheapest commercial nanoparticles in the world production due to their harmless to the human body and environment. Compared with diesel fuel and toluene used above, white oil is a non-irritative and environment-friendly oil phase. In this report we used white oil as oil phase to study how the changes of the wettability of $CaCO_3$ nanoparticles by interaction with sodium stearate induce a double emulsion phase inversion.

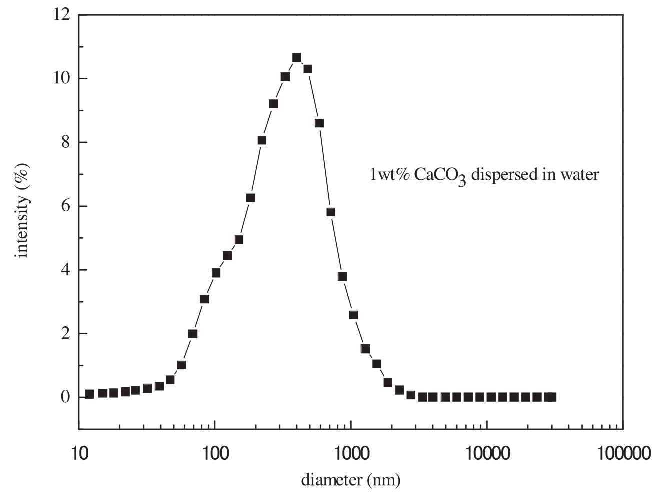

Fig. 1. Size distribution of 1 wt% $CaCO_3$ nanoparticles dispersed in pure water using an ultrasound probe was measured in the laser particle size analyzer (Winner 2000, Jinan Winner Particle Technology Co., China).

2. Materials and methods

2.1. Materials

$CaCO_3$ nanoparticles ($\rho \approx 2.60$–$2.75\ g/cm^3$) with a purity of 98% are produced by a precipitation method and supplied as powders by Chengdu Kelong Chemical Co., Ltd. Fig. 1 shows the size distribution of the particles. Sodium stearate (analytical reagent) and white oil ($8^{\#}$) were purchased from Chengdu Kelong Chemical Co., Ltd (China) and used as received. Ultrapure water used with a resistance of 18.2 MΩ cm at 25 °C was produced from an ultrapure producer (Chengdu Ultrapure Technology Co., China.).

2.2. Methods

2.2.1. Preparation of aqueous dispersions of $CaCO_3$ nanoparticles

1 wt% $CaCO_3$ nanoparticles were dispersed into 50 °C pure water using an ultrasonic dispersing machine (JK-50B, Hefei Jinnick Machinery Manufacturing Co., Ltd.) at 50 w for 3 min. Different amounts of sodium stearate were dissolved into the $CaCO_3$ dispersions and the systems were dispersed using a digital high-speed stirring apparatus (ZNJ-2, Qingdao Tongchun Oil Instrument CO., China.) at 3000 rpm for 3 min.

2.2.2. Zeta potential of aqueous dispersions of $CaCO_3$ nanoparticles

1 wt% $CaCO_3$ nanoparticles were weighed into ultrapure water of different pH values being adjusted using HCl and NaOH at 50 °C. The particles were dispersed using an ultrasonic dispersing machine at 50 w for 3 min. The dispersions were thermostated at 50 ± 0.5 °C for 24 h. The pH was measured using a digital pH meter (PHS-2C, JinTan Jinnan Instrument Manufacturing Co., Ltd.) and the zeta potentials of the $CaCO_3$ nanoparticles were then measured by using a Zeta potential analyzer (Zeta Pals 190 Plus, U.S. Brookhaven).

2.2.3. Preparation and characterization of emulsions

1 wt% $CaCO_3$ nanoparticles were dispersed into 50 °C pure water using an ultrasonic dispersing machine (JK-50B, Hefei Jinnick Machinery Manufacturing Co., Ltd.) at 50 w for 3 min. Different amounts of sodium stearate were dissolved into the $CaCO_3$ dispersions and the systems were then dispersed using a digital high-speed stirring apparatus (ZNJ-2, Qingdao Tongchun Oil Instrument CO., China.) at 3000 rpm for 3 min. An equal volume of white