Chemical Engineering Science 179 (2018) 73–82

Contents lists available at ScienceDirect

Chemical Engineering Science

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

Emulsion behavior control and stability study through decorating silica nano-particle with dimethyldodecylamine oxide at n-heptane/water interface

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HIGHLIGHTS

- Ludox silica nano-particles has a positive effect stabilizing emulsion. The synergism between SNPs and surfactant were studied by multiple methods with the concentration of surfactant as variable.
- Double phase inversion and its influence on emulsion stability were discussed.

ARTICLE INFO

Article history:
Received 4 September 2017
Received in revised form 10 December 2017
Accepted 6 January 2018
Available online 8 January 2018

Keywords:
Silica nano-particles
Cationic surfactant
Emulsion
Interface modification

ABSTRACT

Emulsions have been widely applied in subterranean enhanced oil recovery processes, cosmetics and chemistry engineering fields, etc. Current research interests are focusing on improving the stability of emulsion by involving surfactants or colloidal materials. This work aims to enhance the emulsion stabilization by introducing silica nanoparticles (SNP) surface-hydrophobilized/hydrophilized by adding dimethyldodecylamine oxide (OA-12) and to reveal the dynamic behaviors of such composites on the liquid–liquid interface. The synergistic effect between SNPs and OA-12 in solution and on oil/water interface were studied by measuring the zeta potential, interfacial rheology and emulsion viscoelastic rheology, etc. It was found that the oil/water interface viscoelastic modulus are augmented by modified silica nano-particles and at the same time emulsions acquired significant long-time stability. Furthermore, phase transformation was induced with the increase of the concentration ratio between OA-12 and silica nano-particle, the emulsion type change from o/w, then to w/o and back to o/w. It is suggested that the inversions are induced by the mounting adsorption of OA-12 molecules on SNPs, which changes the hydrophilic-lipophilic balance of particle surfaces.

1. Introduction

Colloid particles, including silica particles, applied for pickering emulsions stabilization have been studied extensively since its discovery in 1907 (Pickering, 1907). It has been applied massively in fields including oil recovery, cosmetics and food industries, etc. (Stuart et al., 2010; Wakefield and Park, 2007).

Recent studies of emulsions stabilized by mixtures of surfactant and nano-particles have focused on their behaviors and properties. Particles of alumina, silica, carbon or barium sulfate have been researched as composites with various surfactants of cationic, anionic or polymeric (Gelot et al., 1984; Lagaly et al., 1999; Gosa and Uricanu, 2002; Legrand et al., 2005; Johansson et al., 1995).

The capability of these surfactant/particle composites on emulsion stabilization depends on the adsorption of surfactants on the particles surface and the particles on the oil/water interface (Mehta et al., 2015). Hassander et al. had studied the mechanism of oil-in-water emulsions stabilized by small silica (Ludox) particles with costabilizers to induce silica particle agglomeration, and proposed a popular stabilization mechanisms: silica particles agglomeration in bulk and adsorption at the oil/water interface (Hassander et al., 1989). Following this case, composite of cetyltrimethylammonium bromide with silica nano-particles/SNPs

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https://doi.org/10.1016/j.ces.2018.01.005
0009-2509/

stabilized emulsions was studied by Binks and Rodrigues. In which, they proved the adsorption of surfactant on particle surface which leads to particle aggregation, and such aggregation had excellent adsorption ability on oil/water interface, which provided emulsions with standout long-term stability as a result (Binks and Rodrigues, 2007).

Lan et al. studied the influence of variable factors on the CTAB and silica nano-particles composite. The effects of salinity, pH, silica nano-particles and CTAB concentration on the stability of emulsions were investigated (Lan et al., 2007). Xu et al. have studied w/o emulsion that was stabilized by a nanoscale single chain "tadpole-like" polymer particles along with its double phase reaction application (Xu et al., 2014). Perino et al. analyzed the influence of fumed silica particles on water-in-crude oil emulsions with multiple methods including stability examinations, interfacial tension measurements, dilatational interfacial rheology tests, shear rheology tests, and Cryo-SEM analysis. It seems mechanisms of emulsion with particles stability were largely influenced according to the particle wettability (Perino et al., 2013). Yazhgur et al. investigated the adsorption film of silica nano-particles modified by CTAB at the air/water interface by dilatational surface rheology and optical investigations. Variable factors like the surface strain and surfactant concentration might cause the surface elasticity reaching an extremely high value when particles aggregate in the dispersions (Yazhgur et al., 2013).

Kundu et al. studied the rheological behavior of surfactant-stabilized oil-in-water emulsions. Factors including temperature, fraction of oil, pH and concentration of anionic surfactant were studied exclusively. Researchers found that oil-in-water emulsions exhibit typical shear thinning behavior and shear stress and shear rate could be well coordinated by the power law and other non-Newtonian fluid models. In one of their studies, Herschel-Bulkley model was applied for analysis of rheological data. The combined effect of volume fraction and temperature on viscosity of emulsions was described with proposed correlation (Kundu et al., 2015, 2017, 2013).

Phase inversion of Pickering emulsions were also reported in literatures. Schulman and Leja explained the linkage between tri-phase contact angle of oil-water-solid interfaces and the preferred emulsion type by studying SDS surface-modified $BaSO_4$ composite. Phase inversion was induced when $BaSO_4$ powder as hydrophilic coated particles was added into oleic acid w/o emulsions. Continuing adding of $BaSO_4$ as hydrophobic coated particles converted o/w emulsions to w/o type (Schulman and Leja, 1954). Tambe and Sharma demonstrated the inversion of emulsions stabilized by calcium carbonate particles that has been surface-modified by stearic acid (Tambe and Sharma, 1993).

Synergism between surfactants and silica particles has been researched with details and depth. Our purpose of this study is to propose a new composite of surfactant and particles, and take insight into phenomena that appeared. Through comparative studies, types and stability were investigated for emulsions stabilized by surfactant surface-modified SNPs or surfactant alone. Zeta potentials, dilatational interfacial rheology tests, rheology and viscoelastic measurements of emulsions were conducted. The aim of our study is to find and prove the adsorption of surfactant OA-12/dimethyldodecylamine oxide onto silica, and hence study the properties of such composite on oil/water surface. OA-12, dimethyldodecylamine oxide, is a pH sensitive cationic/nonionic surfactant. In this study, all experiments were carried out at pH = 6 ± 0.2, when silica nano-particles are mostly negatively charged and dimethyldodecylamine oxide is cationic at this point. It appears the electrostatic attraction between these two components caused adsorption of surfactant molecules on SNPs.

2. Experimental section

2.1. Materials

Ultrapure water with a resistance of 18.25 MΩ was collected from a reverse osmosis unit (ULUPURE, UPT-II-5T). Hydrochloric acid (Sinopharm Chemical Reagent Co., Ltd, China, 36%) and sodium hydroxide (XiLong Co., Ltd, 96%) were used to adjust pH. The cationic surfactant, dimethyldodecylamine oxide (OA-12), was a gift from Shanghai Jianhong Industry., Ltd., with a concentration of 30%wt. The oil phase was n-heptane (Sinopharm Chemical Reagent Co., Ltd, ≥98.5%). The silica nano-particles, LUDOX® HS-30 colloidal silica, was purchased from Sigma-Aldrich as a 30 wt% suspension with a pH of 9.8, surface area of 220 m^2/g and density of 1.21 g/mL at 25 °C. The Ludox HS-30 silica nano-particle dispersion has an average size around 13 nm. The diameter measurement is depicted in Fig. 1.

2.2. Methods

2.2.1. Preparation of aqueous dispersions and solutions

For OA-12-only solutions, OA-12 were diluted into target concentrations in 40 mL glass bottles. For OA-12 in nano-particles dispersions, first, the 30 wt% silica dispersion was diluted to 2 wt% aqueous dispersion with ultrapure water. Then, different portions of OA-12 was weighed into 40 mL glass bottles, then diluted by formerly prepared 2 wt% silica nano-particles aqueous dispersion. The concentration range of surfactant was from 0.014 $mol \cdot L^{-1}$ to 6.568 $mol \cdot L^{-1}$. All dispersions were investigated at pH = 6 ± 0.2. The solutions or dispersions were stirred for ten minutes first and then the pH was lowered to 6 ± 0.2 by addition of HCl/NaOH dilution. Aggregation was measured by height and weight in the order of concentrations. A Malvern Zetasizer HS-3000 instrument was equipped for zeta potential measurements for OA-12 and SNPs composite dispersions. All measurements were repeated twice at least for valid results. Supernatant was taken for measurements for dispersions that have agglomeration. After the stability inspection of different concentrations of OA-12, some of these samples was selected for further investigation of interfacial rheology properties.

2.2.2. Preparation and characterization of emulsions

Equal volumes of oil and water (10 cm^3 each) were prepared in 40 mL glass bottles. Emulsions were prepared with homogenizer with a stirring speed at 10,000 rpm for 4 min. Before homogenization, these dispersions were stabilized for 24 h after pH

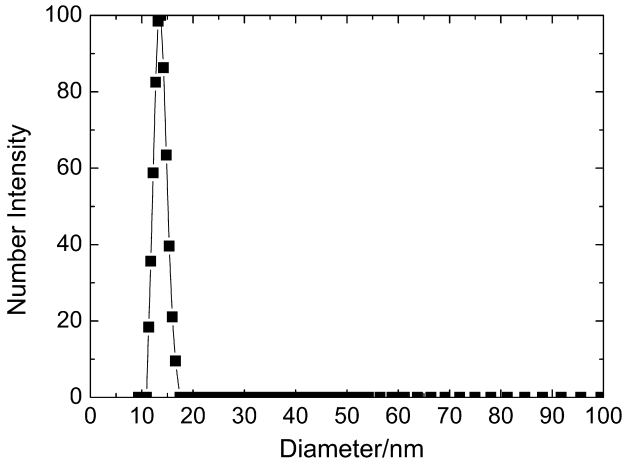

Fig. 1. Diameter distribution of Ludox HS-30 silica nano-particles at pH = 6 ± 0.2.