



Synergistic stabilization of emulsions by poly(oxypropylene)diamine and Laponite particles

Jun Wang^a, Guopeng Liu^{a,b}, Liya Wang^a, Caifu Li^a, Jian Xu^a, Dejun Sun^{a,*}

^a Key Laboratory for Colloid & Interface Chemistry of Education Ministry, Shandong University, Jinan, Shandong 250100, PR China

^b Department of Chemistry, Shandong Institute of Education, Jinan, Shandong 250013, PR China

ARTICLE INFO

Article history:

Received 12 July 2009

Received in revised form 8 October 2009

Accepted 4 November 2009

Available online 10 November 2009

Keywords:

Pickering emulsion

Stability

Laponite particles

Diamines

Adsorption

ABSTRACT

Liquid paraffin–water emulsions were prepared which were stabilized by Laponite particles in situ modified with poly(oxypropylene)diamines in the absence of electrolytes. First, the characteristics of the Laponite dispersions in the presence of increasing concentrations of diamines were studied in detail. Infrared absorption spectra and zeta potential measurements confirm the adsorption of diamines on the Laponite particles. Adsorption isotherms further indicate highly affinitive L-type behaviors and the diamine molecules are deduced to lie with both end groups anchored on the particle surface and the poly(oxypropylene) chain exposed to the aqueous solution. Then, emulsions were prepared using the diamine-modified particles. Diamines and Laponite particles alone are ineffective emulsifiers, but a strong synergism is exhibited between them. Laser-induced fluorescent confocal micrographs and TEM observations demonstrate the arrangement of the particles on the emulsion surfaces and also reveal the stability mechanisms. The emulsion stability was also explored with optical microscopy and droplet size measurements. As the diamine concentration increases, the extent of emulsion creaming decreases and the droplet size correspondingly decreases. At a certain low diamine concentration, the extent of emulsion creaming decreases down to a minimum and the corresponding droplet size is the smallest. This optimal emulsion state is unchanged when the diamine concentration is further increased.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

In addition to using conventional surfactants or surface-active polymers as both emulsifier and stabilizer for macroemulsions of oil and water, colloidal solid particles are also effective emulsion stabilizers, producing the so-called Pickering emulsions [1]. Pickering emulsions are of great practical interest due to their widespread use in many areas including cosmetics, food, pharmaceuticals, oil recovery and wastewater treatment. In many of these applications, good emulsion stability is necessary to maintain the properties of the products over long periods of time. The stability is related to a crucial factor, that is, the wettability of the particles at the oil–water interface. For interfacially adsorbed particles, optimum contact angles (θ) between 70° and 86° and between 94° and 110° have been suggested for the stabilization of oil-in-water (o/w) and water-in-oil (w/o) emulsions, respectively [2,3].

To obtain a stable Pickering emulsion, surfactants are usually added to tailor the wettability of particles, so that their adsorption at the liquid–liquid interface is favored. To date, many kinds of surfactants, whether cationic, anionic, or polymeric have

been used. Recently, Gauckler and coworkers [4] have prepared ultrastable o/w emulsions using colloidal particles modified with short amphiphilic molecules. Binks et al. investigated the stability of emulsions containing silica particles by adding a variety of surface-active materials such as cationic CTAB [5] (cetyltrimethyl ammonium bromide), anionic SDS [6] (sodium dodecyl sulfate), and nonionic surfactants of the C_nE_m (alkylpoly(oxyethylene)) type [7]. Midmore [8] prepared o/w emulsions stabilized with a combination of colloidal silica and nonionic PEO surfactant and found a strong emulsification synergy between the silica particles and the nonionic surfactant. Midmore [9] also prepared very stable o/w emulsions containing silica particles flocculated with homopolymer hydroxypropyl cellulose. The presence of these surfactants enhanced the hydrophobicity of the originally hydrophilic particles, and hence improved the Pickering emulsion stability. All the surface-active materials referred to above are conventional surfactants. Herein, we introduce poly(oxypropylene)diamine molecules as coemulsifiers. Different from the conventional surfactants above, their molecular framework contains two NH_2 groups at both ends of a PPO chain. The diamines are also considered as amphiphilic molecules because they can reduce the oil–water or air–water interfacial tension to some degree. It is important to investigate the properties of diamines because they are expected to be applied in drilling muds and therefore to have an important impact on oil

* Corresponding author. Tel.: +86 531 88364749; fax: +86 531 88365437.
E-mail address: djsun@sdu.edu.cn (D. Sun).

recovery. Lin and coworkers have used these kinds of diamines as intermediates to synthesize another group of complex polymers [10,11], and intercalated the various compounds into layered silicate-type clays [12–14]. The resulting intercalates demonstrated some organophilicity, so we expect that they can also stabilize emulsions.

The other main emulsifier in Pickering emulsions is the solid particles. In previous studies, many kinds of particles have been used as emulsion stabilizers, such as silica, alumina, barium sulfate, calcium carbonate, iron oxides and colloidal metals. Since the clay materials provide a group of solid particles of colloidal size, they are expected to be another kind of promising emulsifier due to their large reserves and low cost. Yan and Masliyah [15,16] have investigated the adsorption of asphaltene treated kaolinite clay particles to the droplet interfaces of o/w emulsions stabilized by such particles alone. Abend et al. [17] similarly reported an increased stability of an o/w emulsion using mixtures of bentonite and layered double hydroxides. Heterocoagulation of both oppositely charged clay particles resulted in non-coalescing emulsions, due to a combination of particulate layers formed around the dispersed droplets and the build-up of a three-dimensional network of particles in the continuous phase, thus reducing the mobility of the emulsion droplets. Lagaly et al. [18,19] have investigated o/w emulsions stabilized by smectite clay particles. Addition of nonionic coemulsifiers modified the wettability of the clay and promoted their enrichment at the oil–water interface. Tsugita et al. [20] have studied the properties of emulsions stabilized by the combination of Na-Montmorillonite and polar organic compounds. Na-Montmorillonite and organic compounds formed insoluble complexes that surrounded the oil droplets, thus stabilizing the emulsions.

In this paper, we chose Laponite particles as a model clay material. They are negatively charged disks. The permanent negative charges of the particles are induced by isomorphous substitution [21]. To our knowledge, very few studies exist in which Laponite particles have been used as stabilizers in preparing Pickering macroemulsions. Ashby and Binks [22] investigated the effect of salt on the preparation of emulsions stabilized solely by Laponite clay particles, but all other reports are of mini- or nano-emulsions [23,24]. We chose to combine poly(oxypropylene)diamine with Laponite to optimize the particle emulsifier. In Lin's work [12–14], the interactions between montmorillonite and diamines were not systematically studied. Especially, the effects of diamine adsorption on the wettability and the electrokinetic properties of the particles have not been reported. So in this study, we first investigated the adsorption properties of diamines on the Laponite surfaces in detail through adsorption isotherms, infrared absorption spectra and zeta potential measurements. Then we prepared a series of paraffin emulsions with Laponite particles alone, diamines alone, and mixtures of particles with diamines. All of the emulsifying agents were initially located in the aqueous phase before emulsification. The arrangement of particles on the emulsion surfaces was confirmed by laser confocal microscopy imaging and TEM. A synergism between the Laponite particles and diamines affected the emulsion stability. Unlike the classical surfactants, only a small amount of diamine is needed to produce an optimal emulsion, and this state will remain unchanged as the diamine concentration is further increased. A synergistic stabilization mechanism is also proposed.

2. Experimental

2.1. Materials

Laponite RD, a synthetic hectorite, was supplied by Rockwood Additives Ltd. (UK) as a white powder. The basic properties of

Laponite have been presented in detail in our previous work [25]. The poly(oxypropylene)diamines obtained from Huntsman Chemical Co. were used as received. They are difunctional, primary amines with average molecular weights of about 230 and 430 (referred as D-230 and D-400 below, respectively). The primary amine groups are located on secondary carbon atoms at the end of the aliphatic polyether chain. The general chemical formula of D-230 is $\text{H}_2\text{NCH}(\text{CH}_3)\text{CH}_2[\text{OCH}_2(\text{CH}_3)\text{CH}]_{2.5}\text{NH}_2$ and the formula for D-400 is $\text{H}_2\text{NCH}(\text{CH}_3)\text{CH}_2[\text{OCH}_2(\text{CH}_3)\text{CH}]_{6.1}\text{NH}_2$. The oil phase was liquid paraffin (Sinopharm Chemical Reagent Co., China) with purity greater than 99% ($d_4^{20} = 0.835\text{--}0.855$). The composition of liquid paraffin is mainly isoalkane and the main carbon number distribution measured with Agilent 6820 GC (Agilent Co., USA) is between 16 and 26. The water was deionized water purified by ion exchange.

2.2. Methods

2.2.1. Preparation of Laponite/poly(oxypropylene)diamine aqueous dispersions

Aqueous dispersions of Laponite with poly(oxypropylene)diamine were prepared by combining stock solutions of the reagents. First, a Laponite stock dispersion (1 wt%) was prepared by dispersing 4 g of Laponite particles into 396 g of deionized water using a Multimixer (Baroid Co., USA). Then, the prepared Laponite dispersion was sealed and laid aside for 1 week before use. After that, 10 ml of diamine solutions (with concentrations ranging from 0.75 to 75 mM) were added to 10 ml of 1 wt% Laponite dispersion to obtain a series of 20 ml mixed dispersions. The pH of the Laponite/diamine aqueous dispersions was adjusted to between 9.5 and 10.5 with NaOH or HCl. The prepared dispersions were stirred for at least 12 h to attain adsorption equilibrium. All experiments were performed at room temperature (25 °C).

2.2.2. Stability of the Laponite/poly(oxypropylene)diamine aqueous dispersions

The prepared Laponite/diamine dispersions were first transferred into a stoppered glass tube with internal diameter 1.6 cm and length 15 cm. Then the phase behavior of the dispersions was observed after 72 h of preparation.

2.2.3. Infrared spectroscopy

Laponite/diamine aqueous dispersions were first centrifuged for 30 min at a speed of 20,000 rpm and the sediment was washed with deionized water three times to remove the unadsorbed diamines. Then, the samples were dried at 80 °C and crushed into powders which were pressed into KBr pellets for infrared spectrometry. The spectra of diamine-modified Laponite particles were measured in transmission mode with a Fourier transform infrared (FTIR) spectrometer (Nicolet 5700, USA). Spectra were taken at 4 cm^{-1} resolution with accumulation of 500 scans for an acceptable signal/noise ratio.

2.2.4. Zeta potential measurements

The zeta potentials of Laponite/diamine dispersions were measured with a JS94H microelectrophoresis instrument (Shanghai Zhongchen Digital Technic Apparatus Co., China). The particles in the lower sediment phase were diluted with the supernatant to make the particles visible under the microscope before measurement.

2.2.5. Adsorption isotherm of poly(oxypropylene)diamine on Laponite particles

The prepared dispersion was centrifuged for 30 min at 20,000 rpm in order to completely separate the clay particles from the supernatant. The concentration of diamines in the supernatant

Download English Version:

<https://daneshyari.com/en/article/595675>

Download Persian Version:

<https://daneshyari.com/article/595675>

[Daneshyari.com](https://daneshyari.com)