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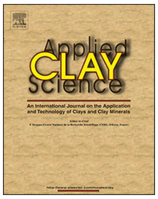

Research paper

Selective modification of kaolinite with vinyltrimethoxysilane for stabilization of Pickering emulsions

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ABSTRACT

Amphiphilically modified kaolinite was produced by the modification of the octahedral surface of kaolinite with vinyltrimethoxysilane for use in the stabilization of Pickering emulsions. The covalent grafting of the hydrolysate of vinyltrimethoxysilane on the kaolinite octahedral surface resulted in kaolinite exhibiting dual-surface affinity. Further, the surface wettability of the modified kaolinite could be tuned by regulating the reaction temperature. Investigations of emulsions stabilized using the modified kaolinite samples indicated that the emulsion stability was significantly higher. In addition, the phenomenon of phase inversion could be controlled based on the wettability of the modified kaolinite. The highest stability of emulsion was observed when the emulsion droplet size was the lowest and the emulsion viscosity was the highest at the phase-inversion point. These findings should lead to the development of methods for preparing amphiphilic surface-active emulsifiers as well as the production of the desired types of emulsions at a given water/oil ratio.

1. Introduction

Emulsions are usually a mixture of two immiscible liquids consisting of an oil phase and aqueous phase, wherein one of the phases is dispersed into the other continuous phase. Emulsions are used in various products and applications such as food preparation and paints (Mayer et al., 2013; Elhalawany et al., 2014). Emulsions can be classified as oil-in-water emulsions (O/W), water-in-oil emulsions (W/O), and multiple-phase emulsions (W/O/W and O/W/O), based on the type of continuous phase. With a change in the phase composition, an O/W (W/O) emulsion can be converted into a W/O (O/W) emulsion. This phenomenon is called phase inversion. The phase inversion of emulsions is of importance with respect to the protection and controllable release of the dispersed phase and finds wide application in food storage, oil recovery, and cosmetics production (Cui et al., 2010; Perazzo et al., 2015).

Surfactants and polymers are conventionally used as emulsifiers for stabilizing emulsions. However, most surfactant-stabilized emulsions are susceptible, owing to their low viscosity. Further, surfactants can be harmful to the environment. Thus, solid particles, such as those of hydrophilic silica or carbon black, have been developed for stabilizing emulsions. Those emulsions stabilized by solid particles are called Pickering emulsions. Nevertheless, unlike surfactant-stabilized emulsions, Pickering emulsions stabilized using solid particles exhibit low stability. In addition, it is difficult to control the phase-inversion phenomenon owing to the lack of dual-surface affinity in these particles (Reger et al., 2012; Nallamilli and Basavaraj, 2017). To overcome these difficulties, amphiphilic surface-active particles have been fabricated for use as an emulsifier, such that the surface adsorption energy of the particles at the water-oil interface is high (Binks and Clint, 2002). However, Pickering particles are usually symmetric. Hence, their modification is nondirective, owing to which the modified particles exhibit homogenous surfaces. Therefore, the selective modification of asymmetric particles for producing amphiphilic surface-active particles has attracted much attention for use in Pickering emulsions (Walther and Muller, 2008; Kaewsaneha et al., 2013).

Kaolinite (Kaol) typically consists of asymmetric particles with two polar basal surfaces, with the external octahedral surface being capped by μ-hydroxy groups (μ-Al_2-OH) and the external tetrahedral surface being capped by siloxane groups (Si—O). However, the polarity of Kaol is usually hidden because the octahedral surface is covered by μ-hydroxy groups while the tetrahedral surface adsorbs a layer of hydrated cations owing to the weak negative counterforce resulting from isomorphous substitution (Brady et al., 1996; Hirsemann et al., 2012;

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Weiss et al., 2013). Modifiers such as dimethyl sulfoxide, methoxy groups,1,2-butanediol, and 1,3-butanediol was used to modify Kaol to transform the surface property (Tunney and Detellier, 1996; Komori et al., 2000; Murakami et al., 2004). However, these various modifiers were intercalated the interlayer surface of Kaol by nondirective modification, which was not efficient to stabilize emulsions owing to lack of amphipathic groups. To overcome this challenge related to the hidden polarity of Kaol, the selective modification of the Kaol surface has been proposed. For example, Hirsemann et al. (2012) reported the selective decoration of Kaol platelets by the selective modification of their tetrahedral and octahedral surfaces through the covalent grafting of catechol and cation exchange with a $[Ru(bpy)_3]^{2+}$ complex (bpy = 2,2′-bipyridine), respectively. After this selective decoration process, the Kaol sample exhibited the desired polarity and could be used to successfully increase the stability of emulsions. However, the selective and individual modification of the tetrahedral and octahedral surfaces of Kaol remains a challenge. Further, the increase in the polarity of Kaol is limited because the modification process eventually reaches a point of saturation. Therefore, it would be highly desirable to develop an efficient modifier for selectively modifying one of the Kaol surfaces and hence the regulation of the wettability of Kaol.

In this study, vinyltrimethoxysilane (VTMS) was chosen as a modifier to selectively modify the aluminum-oxygen octahedral surface of Kaol, as the silicon hydroxyl groups of VTMS hydrolysate match the aluminum-oxygen octahedral surface of Kaol in length. Further, the self-condensation polymerization of the silicon hydroxyl groups prevented the modification process from plateauing, thus not only turning the Kaol octahedral surface hydrophobic but also allowing for the tuning of the wettability of the modified Kaol sample. Finally, the modified Kaol samples were used to stabilize Pickering emulsions, whose phase-inversion behaviors were investigated.

2. Experimental section

2.1. Materials

Sodium chloride (analytical grade), liquid paraffin (chemical grade), hydrochloric acid (analytical grade), and ethanol (analytical grade) were provided by Xilong Chemical Co., Ltd. and were used as received. VTMS (98%) was obtained from Macklin Biochemical Co., Ltd. Pristine Kaol (Maoming, China) was purified by sedimentation and the < 2 μm fraction was collected using the standard procedure (Hirsemann et al., 2012). Deionized water produced using a reverse osmosis unit with Axlwater (AXLB1015) was used in all the experiments.

2.2. Methods

2.2.1. Modification of kaolinite surface

First, 2 g of the pristine Kaol was dispersed in a mixture of 35 mL of ethanol, 5 mL of hydrochloric acid (1 mol/L), and 15 mL of deionized water and stirred for 15 min at room temperature. This was followed by the dropwise addition of 4 mL of VTMS into the dispersion. Then, the dispersion was stirred at 40°C for 10 h. The obtained slurry was centrifuged and washed five times with a mixture of 35 mL of ethanol and 15 mL of deionized water to remove the unreacted reagents and then dried at 70 °C in a drying oven for 48 h to obtain the modified Kaol sample. This modified Kaol sample was labeled as gKaol-40. Similarly, the Kaol samples prepared at 50, 60, 64, 67, 70, and 80 °C were labeled as gKaol-50, gKaol-60, gKaol-64, gKaol-67, gKaol-70, and gKaol-80, respectively.

2.2.2. Preparation of Pickering emulsions

Initially, 0.25 g of the modified Kaol sample in question (emulsifier) was added to 8 mL of liquid paraffin and stirred for 5 min for use as an oil liquid matrix. An aqueous phase consisting of 17 mL of a 1 mol/L NaCl solution was added to the oil liquid matrix, and the mixture was placed in a thermostat (DF-101S) under stirring at a rate of 1300 rpm for 10 min. After being stirred, the emulsion was transferred to a test tube and left to stand for 10 min. The volume fraction of the liquid-paraffin phase ($\phi_o = V_{oil}/(V_{oil} + V_{water})$) was regulated by varying the initial volumes of the liquid-paraffin and aqueous phases (water/oil ratio). Further, the type of emulsifier (modified Kaol) used were also varied for different request of emulsions.

2.3. Characterization

The degree of wettability of the unmodified (Kaol) sample as well as those of the various modified Kaol samples were assessed using an optical water contact angle meter (SL200KS, Kino industry Co., Ltd., USA). The powder sample in question (0.1 g) was pressed at 10 MPa for 20 s to form a slice, which was then immersed into liquid paraffin at room temperature. Then, a single water droplet (6 μL) was dropped onto the sample surface, and the three-phase contact angle was measured. Fourier transform infrared (FTIR) spectroscopy was performed with a Thermo Nexus 470 infrared spectrometer using the KBr disk technique. The reflection spectra of the modified Kaol samples and the absorption spectrum of VTMS were recorded using an ultraviolet-visible-near infrared spectrometer (UV 3600). X-ray diffraction (XRD) analysis, performed using a PANalytical X'pert PRO powder diffractometer equipped with a Cu-K_α radiation source (λ = 0.15405 nm), was employed to determine the structures of the various samples at 40 KV and 40 mA. The Si/Al mass ratios of the unmodified and modified Kaol samples were determined using a field-emission scanning electron microscopy (FESEM, Hitachi S-4800) system with an energy-dispersive X-ray spectroscopy (EDS) attachment. The operating voltage was 15 kV, and the working distance was 15 mm. Thermogravimetric analysis (TGA) was carried out in a PerkinElmer STA 8000 system under dynamic heating conditions (10 °C/min) between 30 °C and 800 °C in a nitrogen flow of 20 mL/min. Optical micrographs of the various emulsions were obtained using a Nikon Eclipse E200 polarizing microscope fitted with a DS-Fi2 camera, while digital photographs were taken with a Canon Power Shot G7X camera. The conductivities of the emulsions were measured using a DDSJ-308F digital conductivity meter with a DJS-1D Pt/Pt black electrode (Leici Co., China). The viscosities of the emulsions were determined using a NDJ-8S digital viscosity meter (Lichen Co., China) with a No. 3 rotor at 60 rpm.

3. Results and discussion

The chemical structure and surface properties of modified Kaol are the primary factors determining emulsion stability as well as the related phase-inversion behavior. FTIR is an effective method for analyzing the structure of modified Kaol. In the infrared spectrum of Kaol (unmodified sample), bands related to the stretching vibrations of the μ-hydroxy groups and the inner hydroxyl groups of Kaol were detected at 3694 cm^{-1} and 3619 cm^{-1}, respectively (Hoch and Bandara, 2005), as shown in Fig. 1a. On comparing the hydroxyl stretching vibration bands of gKaol-60 with those of Kaol, it was found that the full width at half maximum (FWHM) of the peak corresponding to the μ-hydroxy stretch vibrations of gKaol-60 at 3702 cm^{-1} was greater than that of the corresponding peak in the case of Kaol. Further, the peak in the former case was shifted to a higher wavelength, suggesting that the reaction of μ-hydroxy and VTMS resulted in a change in the length and energy of the Al-OH bond. The same phenomenon, namely, an increase in the FWHM, was also observed in the case of the peak related to the Al-O-Si flexural vibrations at wavenumbers of 468–537 cm^{-1} (Fig. 1c). This result can be ascribed to the presence of a new chemical bond (Al—O—Si bridge) resulting from the grafting of VTMS on the Kaol octahedral surface. Furthermore, peaks corresponding to the trimethoxysilane groups were seen at 1099 cm^{-1} and 1197 cm^{-1} (Ahmed et al., 2009; Qin et al., 2015). The absorption peak of the Si–OCH_3 group at