Colloids and Surfaces A: Physicochem. Eng. Aspects 431 (2013) 133–141

Contents lists available at SciVerse ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Effect of polyisobutylenesuccinimide on low-temperature rheology and dispersibility of clay particles in mineral oil

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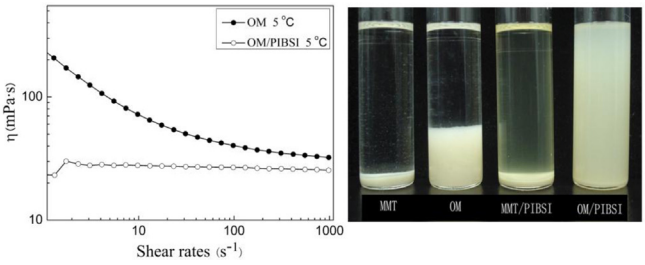
HIGHLIGHTS

- Low-temperature viscosity of organoclay dispersions can be reduced by PIBSI.
- Low-temperature dispersibility of organoclay was largely improved by PIBSI.
- PIBSI has little impact on the long-term stability of montmorillonite.
- PIBSI adsorbs on the surface of organoclay by hydrogen bonding.
- PIBSI provides steric effect and modifies the Hamaker constant of organoclay.

GRAPHICAL ABSTRACT

Polyisobutylenesuccinimide (PIBSI) can significantly reduce the viscosity and improve dispersibility of organoclay dispersions in mineral oil at low temperatures. In contrast, PIBSI has no significant effect on long-term stability of montmorillonite. In these figures, OM represents organoclay and MMT indicates montmorillonite.



ARTICLE INFO

Article history:
Received 22 January 2013
Received in revised form 21 March 2013
Accepted 12 April 2013
Available online 25 April 2013

Keywords:
Low temperature
Clay
Dispersion
Nonpolar solvents
Polyisobutylenesuccinimide

ABSTRACT

In the process of deepwater drilling, maintaining proper low-temperature rheological properties of oil-based drilling fluids and controlling the viscosity of clay dispersions in nonpolar solvents are of great importance. In this work, a dichain polyisobutylenesuccinimide with sufficient viscosity lowering performance was synthesized. The effects of polyisobutylenesuccinimide on low-temperature rheology and dispersibility of organoclay particles in mineral oil were investigated by rheological measurements, sedimentation experiments, optical microscopic observation and transmission electron microscopy. The results indicate that the polyisobutylenesuccinimide is an effective rheological modifier and dispersant at low temperatures in nonpolar solvents. The dispersion mechanism was investigated by Fourier transform infrared spectroscopy, adsorption measurements and X-ray diffraction. The results suggest that the polyisobutylenesuccinimide molecules adsorb on the surface of organoclay particles by hydrogen bonding interactions. The combination of steric stabilization and modification of the Hamaker constant of the particles leads to stable organoclay dispersions. In contrast, polyisobutylenesuccinimide has no significant impact on the long-term dispersibility of unmodified montmorillonite in mineral oil, because of the lower surface coverage.

1. Introduction

Dispersions of particles in nonpolar media have a diverse range of applications in our daily life, such as inks [1,2], paints and coatings [3,4], ceramics [5], cosmetic formulations, lubricants [6–8], and drilling fluids [9]. In particular, investigations on the behavior of nonaqueous dispersions of organoclay provide a theoretical basis for the preparation of clay–polymer composites [10–12] and the application of oil-based drilling fluids [4,13].

Nonaqueous dispersions of organoclay are an important part of the oil-based drilling fluids and can modify the viscosity and shear force of drilling fluids. However, high pressure and low temperature

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http://dx.doi.org/10.1016/j.colsurfa.2013.04.034

are often encountered in the process of deepwater drilling. It is difficult to control the rheological properties of the drilling fluids at low temperatures, so it is essential to study the low-temperature rheological properties and dispersion stability of clay in nonpolar solvents. Generally, the dispersions of particles in nonpolar solvents are unstable, and phase transition phenomenon often appears at lower temperatures, which leads to a significant increase in the viscosity. Wagner and co-workers have carried out a series of research on the phase transition [14–16]. Octadecyl-coated silica particles were dispersed in tetradecane and oscillatory shear rheological measurements were used to investigate the phase transition [14]. When the temperature is above 31 °C, the dispersion is a fluid with a negligible elastic modulus G'. But as the temperature falls, the system turned into a viscoelastic gel. In the narrow range of 29–27 °C, the G' greatly increases. They believe that the octadecyl and solvent molecules are in a state of random arrangement above the gelation point. As the temperature drops, the molecules become straight and ordered. A dense crystalline layer is formed and the change in density increases the van der Waals attraction, which leads to particle aggregation and dispersion gelation [15]. Therefore, the viscosity of the dispersions sharply increases.

The addition of dispersants can solve the problem of the increase in viscosity of particle dispersions in nonpolar solvents. The dispersants can adsorb on the surface of particles and provide steric stabilization or electrostatic repulsion, which in turn improves the stability of the dispersions [17]. Because of the low ionic concentration and dielectric constant in nonpolar media, it is difficult for particles to be charged and the electrostatic force is immeasurably weak. Therefore electrostatic repulsion is less effective in nonpolar solvents. However, steric stabilization is effective both in aqueous and non-aqueous dispersions and is generally believed to play a major role in nonpolar solvents [18–21]. Pure steric stabilization must meet the following two conditions [17,18]. First, the dispersant must have strong affinity for the particle surface. Second, the chains of dispersant molecules must be long enough to keep the particles apart within a distance of 10–20 nm. In addition, the Hamaker constant of the particles is modified by the adsorbed dispersant, which in turn leads to a weaker van der Waals attraction. The combination of steric stabilization and modification of the Hamaker constant results in stable dispersions in nonpolar solvents.

Polyisobutylenesuccinimide (PIBSI) is a commonly used dispersant in nonpolar solvents. The polar polyamine parts in the middle of the molecule strongly anchor onto the particle surface and the polyisobutylene chains extend into the nonpolar medium providing a steric stabilization for particles [22,23]. Due to the strong adsorption capacity of the polar group, and the good compatibility between the polyisobutylene tails and the nonpolar medium, PIBSI is of high dispersion efficacy over a wide range of temperatures [24]. Therefore it is often used as lubricant and fuel additives to disperse carbon black [21,25–28]. Fowkes and co-workers [25–27] studied the effect of a commercial polyisobutylenesuccinimide (OLOA 1200) on the dispersibility and stability of carbon black in hydrocarbons. They suggested that the interaction mechanism was a combination of electrostatic and steric stabilization. However, Georges et al. [29] measured the repulsive force between PIBSI coated carbon surfaces using a surface force apparatus. The results showed that the PIBSI only supplied steric stabilization and electrostatic repulsion did not exist in the system, which provided a theoretical basis for understanding the interaction mechanism of PIBSI used as lubricant additives.

While PIBSI is widely used to disperse carbon black in nonaqueous media, less attention has been paid to clay particles stabilized by PIBSI [30,31]. van Duijneveldt and co-workers [32] applied PIBSI to disperse laponite and montmorillonite particles for the first time. The results demonstrated its good dispersion effect. However, particular emphasis was placed on the macroscopical dispersal results, and the adsorption and dispersion mechanism are still not well understood. In our previous work [33], the effect of low-molecular-weight nonionic surfactant (Span 80) on the dispersion stability of organoclay has been investigated. In the present study, we synthesized a kind of polymer PIBSI to modify the low-temperature rheological properties of organoclay and montmorillonite dispersions in mineral oil. The effect of PIBSI on the dispersibility of these two types of clay at low temperatures was also investigated by sedimentation experiments. The results indicate that the dispersion effect for organoclay is better than that for montmorillonite. Optical microscopic observation, transmission electron microscopy, Fourier transform infrared spectroscopy, adsorption measurements and X-ray diffraction were performed to further demonstrate the adsorption mechanism of PIBSI on the surface of organoclay and the dispersion mechanism of organoclay in nonpolar solvents.

2. Experimental

2.1. Materials

Sodium montmorillonite (labeled as MMT) was collected from Xinjiang Province of China. The details of the clay and the purification process were described in our previous paper [34]. Dimethyldioctadecylammonium chloride was purchased from J&K Scientific Ltd. Ethanol, hexane, tetrahydrofuran and xylene (analytically pure) were obtained from Shanghai Guangnuo Technology Co., Ltd., China. Octane (analytically pure) was supplied by Tianjin Kermel Chemical Reagent Co., Ltd., China. Ethyl acetate and petroleum ether (analytically pure) were bought from Tianjin Guangcheng Chemical Reagent Co., Ltd., China. Sorbitan monoleate (Span 80, chemically pure) was purchased from Sinopharm Chemical Reagent Co., Ltd., China. Polyisobutylene (M_n = 954 g mol^{-1}) with a α-double bonds content of 85% was received from BASF-YPC Co., Ltd. Maleic anhydride (analytically pure) was purchased from Tianjin Damao Chemical Reagent Co., Ltd., China. Tetraethylenepentamine was obtained from Acros. Mineral oil (Marcol 52) was obtained from Exxon Mobil. The mineral oil is a mixture of alkanes, and the carbon number ranges from 15 to 26, measured with an Agilent 7890 gas chromatograph (Agilent Co.). All the reagents were used as received without further purification.

2.2. Methods

2.2.1. Synthesis and characterization of PIBSI

PIBSI was prepared by a two-step synthesis method as previously described [22,35,36]. The general synthesis scheme is presented in Fig. 1.

2.2.1.1. Synthesis and purification of polyisobutylene succinic anhydride (PIBSA). Polyisobutylene with an average molecular weight of 954 and maleic anhydride were added into a three-necked flask. The molar ratio of the two reagents was 1:1.5. The mixture was stirred and preheated to 50–80 °C, and then the reaction was continued for 6 h at 200 °C in an atmosphere of nitrogen. After the reaction, the solution was cooled to room temperature under nitrogen. The crude product was dissolved with hexane, and the excess of maleic anhydride precipitated after vacuum filtration. After the hexane was distilled off, the product was dried in a vacuum oven at 80 °C overnight. The unreacted polyisobutylene was removed by column chromatography using a volume ratio of 10:1 hexane/ethyl acetate as the eluant. Then the polar tetrahydrofuran was used to wash out the pure PIBSA from the silica gel column.