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Colloidal properties of montmorillonite suspensions modified with polyetheramine

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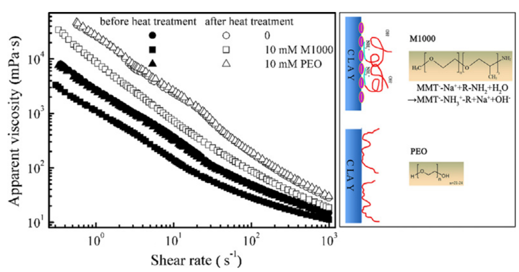
HIGHLIGHTS

- The salt stability of MMT dispersions is improved slightly by adsorbing M1000.
- M1000 maintains the stability of the high temperature treated MMT suspensions.
- PEO causes a weak bridging flocculate for MMT suspensions at high temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, a systematical evaluation of a polyetheramine (Jeffamine M1000) and polyethylene oxide (PEO), which have a similar number of ethylene oxide units and molecular weight, on modulating colloidal stability of montmorillonite suspensions after the high temperature treatment (120 °C, 16 h) or in the presence of salt was performed at 25 °C. A varied of methods including measurement of adsorption, X-ray diffraction (XRD), zeta potential, transmission electron microscopy (TEM), settlement experiments and rheology measurements were used to illustrate the difference. Results indicate that M1000 molecules adsorb onto the particles mainly through an ion exchange mechanism and adopt a densely packed mushroom configuration on the clay surface. Because of the adsorption properties of M1000, the salt tolerance is improved slightly (from 10 mmol/L to 50 mmol/L NaCl) and the colloidal stability of the high temperature treated suspensions is maintained. Meanwhile, PEO molecules adsorb onto clay via hydrogen bonding and take a compact conformation on the clay surface, which could not improve the salt tolerance effectively and leads to a weak bridge flocculation at high temperature. Thus, this finding not only provides some new guidance on modulating the colloidal stability of dispersions but also would be very useful in specific applications, such as drilling fluids and water treatment.

1. Introduction

In recent years, the suspensions of the colloidal plate-like clay particles have been the subject of intense investigation, which are used in variety of applications including drilling fluids [1], paints [2], water treatment [3], drug delivery [4], etc. In several of these suspensions, polymers are usually added to modulate the interactions between colloidal particles. Through careful control of their interaction forces, colloidal clay suspensions can be prepared in the dispersed, weakly flocculated or strongly flocculated states to achieve their practical application [5,6].

Among the variety of clay minerals, montmorillonite (MMT) is a widely used type of smectite clay, with a large surface area, negative surface charge, and ability to swell in water [7,8]. Due to the

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existence of silanol groups and negative charges on MMT surfaces, nonionic polar polymers and cationic polymers are usually used as additives, which may consequently change the colloidal stability and rheological properties of clay suspensions [9–12]. For instance, low molecular weight synthetic ethylene-oxide based nonionic polymers were found to exhibit an inhibiting effect on the dispersion of shale cutting by competing with water molecules for adsorption sites on the clay [10]. Polycations were traditionally used for facilitating clay stabilization and improving debris suspension capacity by forming a protective or encapsulating layer on the surface of the shale [12]. However, most of organic additives or conventional polymers added into MMT suspensions were unstable at high temperature or under salt conditions, which caused deterioration of the rheological properties of clay suspensions. This is disadvantageous for practical applications such as drilling fluids and water treatment where high temperature or salt conditions are frequently encountered [12,13]. Thus, it is of particular importance for finding out the suitable polymers which maintain the colloidal stability of dispersions exposed to high temperature or under salt conditions.

Polyetheramines possessing low molecular weight and well water solubility are attracting increasing attention, because they exhibit a prominent combination of excellent inhibitive performance, heat tolerance, environmentally benign character, and compatibility with drilling fluid formulations [14–16]. Polyetheramines, usually used as interacting agents to obtain inorganic–organic nanocomposites, have not been applied to clay-swelling inhibitors until the early 2000s [17,18]. To the best of our knowledge, much less attention has been devoted to the effect that polyetheramines exert on the colloidal behaviors of MMT suspensions. Cui et al. [19] have reported a systematic investigation on the adsorption of polyetheramines on montmorillonite and elucidated their adsorption mechanism. Recently, they have resurveyed the effect of a polyetheramine on modifying the structure and flow behavior of montmorillonite suspensions at room temperature [20]. Our previous work claimed that the adsorption of poly(oxypropylene) diamine with molecular weight about 230 (D230) could inhibit the dispersion of clay mineral [16]. However, the thorough investigation of polyetheramines on the stability and rheological properties of clay suspensions exposed to high temperature or salt conditions has not yet been reported.

In this work, the effect of Jeffamine M1000 on modulating the colloidal stability of MMT suspensions exposed to high temperature or salt conditions was systematically studied. PEO containing the similar number of ethylene oxide units and molecular weight was investigated to explore how the primary amine group affects the colloidal stability in aqueous solutions. For obtaining the thorough recognition, this work was to determine the adsorption of M1000 and PEO onto MMT particles, elucidate their configuration on the clay surfaces and study the clay particle–particle interactions in their presence using rheological measurements. After that, the effect of M1000 on the colloidal stability and rheological behavior of MMT suspensions exposed to high temperature or NaCl conditions was compared with that achieved using PEO. Our work focuses on the different influences of M1000 and PEO on MMT suspensions at different situations to understand the mechanism of actions, and consequently provide a theoretical guidance on modulating the colloidal stability of dispersions.

2. Experimental

2.1. Materials

Sodium montmorillonite (MMT, Xinjiang Province, China) was used here. The purification and fractionation of the clay were described in details in our previous work [16]. The cationic exchange capacity (CEC) of the clay is 120.8 mmol/100 g. It was characterized using the method of exchanging with ammonium ions described in Handbook of Clay Science [21]. Jeffamine M1000 (referred to as M1000) is a polyetheramine with a molecular structure of $CH_3[OCH_2CH_2]_{19}[OCH_2(CH_3)CH]_3NH_2$ and was obtained from Huntsman. PEO was supplied by Aldrich Chemical Co. Ltd. with molecular weight of 1000 g/mol, whose formula is $H(OCH_2CH_2)_{22.7}OH$. All the reagents were used as received. The water was deionized water purified by ion exchange.

2.2. Methods

2.2.1. Adsorption measurements

The adsorption isotherm was carried out by depletion method as described by Flood et al. [22]. Polymer stock solutions were prepared, mixed MMT stock dispersions and deionized water to prepare 0.5 wt% MMT suspensions with different polymer concentrations. The samples were shaken for 24 h at 25 °C to allow the adsorption to reach equilibrium. After centrifugation at 13,000 rpm for 20 min, the supernatant was diluted within the measuring range of the instrument. Thereafter, the concentration of polymers in the supernatant was determined by TOC-V_{CPN} Total Organic Carbon Analyzer (Shimadzu, Japan). The adsorbed amount was calculated from the difference between the initial and equilibrium concentrations. Under these conditions, the MMT suspensions dispersed with M1000 molecules exhibited a pH range from 8.0 to 10.5, whereas those prepared with PEO displayed a pH of approximately 8.0.

2.2.2. X-ray diffraction

MMT suspensions were mixed with polymer solutions to prepare 0.5 wt% MMT dispersions with different polymer concentrations. The mixed samples were shaken for 24 h at 25 °C to reach the equilibrium. Subsequently, the sediments were collected through centrifugation at 13,000 rpm for 20 min and were washed three times with deionized water to remove still unbound polymer. Finally the sediments were dried at 105 °C and crushed into powders. The powder obtained was analyzed using a D/max-rA (Rigaku, Japan) equipped with a rotating anode under conditions that Cu K_α X-ray radiation was operating at 40 kV and 40 mA. X-ray diffraction (XRD) patterns were collected with 2θ between 2° and 70° using a scanning step of 8°/min.

2.2.3. Zeta potential measurements

The zeta potentials of 0.2 wt% MMT suspensions with different polymer concentrations were measured using a ZetaPALS Zeta Potential Analyzer instrument (Brookhaven, USA).

2.2.4. Sedimentation of MMT dispersions

Sedimentation experiments were performed to investigate the different concentrations of NaCl on the colloidal stability of 0.2 wt% MMT dispersions with 10 mmol/L polymer (M1000 or PEO). In this case, the concentration of NaCl in solutions was varied between 0 and 100 mmol/L. The dispersions were shaken for 24 h at 25 °C, and then transferred into a stoppered glass tubes (with inner diameter 2.0 cm, length 12 cm). Then the phase behavior of the dispersions was observed after quiescence for 24 h at 25 °C.

2.2.5. Transmission electron microscopy

TEM characterizations were carried out to observe the micromorphology of MMT particles with and without polymers when exposed to high temperature. The sample dispersions were placed in an aging cell, and then in an oven at 120 °C for 16 h. The TEM samples were prepared by dipping the prepared dispersions onto carbon-coated copper TEM grids. After the samples were dried, the