



Research paper

In situ ion induced gelation of colloidal dispersion of Laponite: Relating microscopic interactions to macroscopic behavior



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ARTICLE INFO

Article history:

Received 18 August 2016

Received in revised form 22 December 2016

Accepted 23 December 2016

Available online xxxx

Keywords:

Clay dispersion

Laponite dispersion

Rheology

DLVO theory

Inter-particle interactions

ABSTRACT

Aqueous dispersion of Laponite, when exposed to CO₂ environment leads to in situ inducement of magnesium and lithium ions, which is, however absent when dispersion is exposed to air. Consequently, in the rheological experiments, Laponite dispersion preserved under CO₂ shows more spectacular enhancement in the elastic and viscous moduli as a function of time compared to that exposed to air. By measuring concentration of all the ions present in a dispersion as well as change in pH, the evolving inter-particle interactions among the Laponite particles is estimated. DLVO analysis of a limiting case is performed, wherein two particles approach each other in a parallel fashion – a situation with maximum repulsive interactions. Interestingly it is observed that DLVO analysis explains the qualitative details of an evolution of elastic and viscous moduli remarkably well thereby successfully relating the macroscopic phenomena to the microscopic interactions.

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1. Introduction

The macroscopic properties of the colloidal dispersions are determined by various factors that include the nature, the shape and the size distribution of the particles, their concentration, the distribution of charges on the same, etc. (Israelachvili, 2010). These factors in turn determine the entropic considerations as well as the energetic interactions among the particles. With respect to the energetic interactions, while the change in pH determines the nature and the magnitude of the charges on a particle surface, gradual increase in the ionic concentration leads to progressive shielding of the surface charges (Russel et al., 1989). In the present work a colloidal dispersion of Laponite, a disk shaped nanoparticle, in water is studied wherein many of the above mentioned factors are present. An aqueous dispersion of water shows spectacular enhancement in viscosity and elasticity as a function of time, and origin of this behavior has been a subject of intense investigation over past two decades (Angelini et al., 2014; Atmuri and Bhatia, 2013; Jonsson et al., 2008; Morariu and Bercea, 2012; Ruzicka and Zaccarelli, 2011; Shahin and Joshi, 2012a). However, unlike many naturally occurring clay minerals, Laponite is vulnerable to chemical degradation when exposed to acidic environment (Jatav and Joshi, 2014a; Mouchid and Levitz, 1998; Thompson and Butterworth, 1992), usually caused by dissolution of atmospheric carbon dioxide. Under such conditions, Laponite releases various kinds of ions in the aqueous media in which it is suspended (Jatav and Joshi, 2014a). In addition, pH of the dispersion also shows time dependent evolution. Both these in situ effects

gradually alter the electrostatic interactions among the Laponite particles.

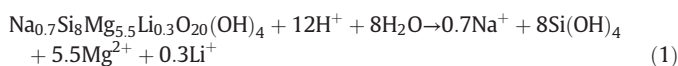
Laponite is 2:1 is a synthetic clay mineral belonging to a family of hectorite with a chemical formula of the unit cell: Na^{+0.7}[(Si₈Mg_{5.5}Li_{0.3})-O₂₀(OH)₄]^{-0.7} (Laponite Technical Bulletin, 1990). In Laponite two sheets of tetrahedral silica sandwich octahedral sheet of magnesia leading to a single particle of Laponite having disk like shape with 25 ± 2.5 nm diameter and 0.92 nm thickness (Kroon et al., 1996). In the middle sheet, lithium isomorphically substitutes magnesium leading to deficiency of positive charge rendering outer two faces of Laponite a negative charge, which is compensated by sodium ions. The edge of a Laponite disk is composed of broken bond and is dominated by Mg–OH, whose point of zero charge is around 12.5 (Stumm, 1992). Consequently, below this pH, the edge acquires a positive charge. As a result, in an aqueous medium with pH around 10, Laponite particles share edge – to – face attraction while face – to – face repulsion. Both these interactions contribute to structural build up in Laponite dispersion, which causes viscosity and elasticity of the dispersion to show spectacular increase when Laponite is dispersed in water (Joshi, 2007). In-corporation of salt in aqueous dispersion of Laponite is observed to enhance the rate at which viscosity and elasticity of the same increases (Shahin and Joshi, 2012b). Such accelerated increase has been attributed to shielding that the dissociated ions provide to the charged faces of a disk, thereby reducing repulsion among the particles. This causes reduction in the repulsive barrier height for the particles to approach each other leading to faster structural build-up (Mongondry et al., 2005; Shahin and Joshi, 2012b).

While Laponite has been in use in variety of industrial applications and in academic studies, Laponite is susceptible to chemical degradation when exposed to acidic environment. Many groups have investigated

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the chemical stability of hectorite over the past few decades (Kerr et al., 1956; Kreit et al., 1982; Tiller, 1968), wherein H^+ ions have been suggested to react with clay mineral causing Mg^{2+} ions to leach. Typically, H^+ ions have been proposed to attack the clay mineral particles at two locations: the faces and the edges (Kerr et al., 1956; Tiller, 1968). It has been conjectured that H^+ ions get adsorbed on the negatively charged faces and eventually penetrate the tetrahedral silica sheet to react with octahedral magnesia sheet (Kreit et al., 1982). The attack on the edges, instead, is more direct. Since the former case involves two steps – the adsorption followed by the penetration – before the reaction takes place (Kreit et al., 1982), it is believed to be slower than the latter (Kerr et al., 1956; Tiller, 1968). In the presence of weak acids, on the other hand, it has been claimed that H^+ ions primarily attack the edges (Kerr et al., 1956). Interestingly Kreit et al. (1982) reported that presence of salt stabilizes the clay mineral, which they attribute to shielding of the clay mineral particles by cations against H^+ ions attack.

The chemical stability of Laponite was investigated for the first time by Thompson and Butterworth (1992) who claimed that degradation occurs when pH of a dispersion decreases below 9. They proposed that Laponite reacts with acid to undergo the following reaction (Thompson and Butterworth, 1992):



Mourchid and Levitz (1998) studied relaxation dynamics of dispersions preserved under air and N_2 atmosphere. Interestingly they observed that samples preserved under air underwent gelation while that of kept under N_2 atmosphere did not. Mourchid and Levitz (1998) attribute this observation to dissolution of CO_2 present in air, which causes leaching of Mg^{2+} and Li^+ ions enhancing the ionic strength of the dispersions. They proposed that increase in concentration of Mg^{2+} and Li^+ ions is responsible for accelerated aging of Laponite dispersion. Jatav and Joshi (2014a) carried out a systematic study wherein they exposed the Laponite dispersions with varying concentrations of Laponite and salt to air atmosphere. They observed that dispersions with high concentration of Laponite and/or that of salt do not show traces of leached Mg^{2+} ions suggesting that the cations associated with a salt as well as the counter-ions provide a stabilizing effect against H^+ ions attack. Very recently Mohanty and Joshi (2016) proposed a chemical stability phase diagram which separates the chemically stable region from that of the unstable region as a function of time with respect to concentration of Laponite and that of salt.

The faces of the disk/plate shaped particles of clay minerals experience repulsive interactions due to their negatively charged nature, while experience attraction due to van der Waals interactions. As a result, historically this system has been studied as a model candidate for an application of DLVO theory (Van Olphen, 1977), which accounts for electrostatic as well as van der Waals interactions among the particles (Israelachvili, 2010). While applying the theory the two negatively charged flat plates of Laponite particles are considered to approach each other in a parallel fashion. This parallel configuration, which, while is only one of the possible configurations, provides information about the maximum repulsive interactions, therefore rendering a qualitative insight. In case of Laponite DLVO theory has been employed to infer about how the microstructure of Laponite dispersion gets affected by concentration of Laponite (Saha et al., 2015; Shahin and Joshi, 2012b), that of externally added salt (Saha et al., 2015; Shahin and Joshi, 2012b), concentration of counterions (Jatav and Joshi, 2016), temperature (Saha et al., 2015; Shahin and Joshi, 2012b) externally added polymers leading to steric interactions (Sun et al., 2012), etc. It has been observed that DLVO theory predicts the qualitative dynamics originating from the interparticle interactions very well.

This work studies effect of Mg^{2+} ion leaching by systematically exposing Laponite dispersion to the CO_2 environment. Furthermore, spontaneous evolution of Laponite dispersion with and without in situ Mg^{2+}

ion leaching is analyzed using rheology and DLVO theory, wherein the latter involves consideration of multivalent cations. This work, on the one hand studies how the macroscopic rheological behavior changes as a function of time, while on the other hand, how the microscopic inter-particle interactions get altered with time. The objective of this work is to relate time evolving microscopic inter-particle interactions to the macroscopic rheological behavior of an aqueous dispersion of Laponite due to in situ change in the ionic concentration.

2. Material, sample preparation and experimental procedure

In order to prepare aqueous dispersion, Laponite XLG® (BYK Additives Inc.) was dried for 4 h at 120 °C. Before mixing Laponite with ultra-pure water (resistivity 18.2 MΩ cm) its pH was maintained at 10 by adding NaOH and molarity was fixed at predetermined value by adding NaCl. The mixing of Laponite and water was carried out for 45 min using Ultra Turrex drive, which leads to clear and colorless dispersion. In this work 2.8 mass% Laponite dispersion was studied with no externally added salt (0.1 mM Na^+ ion concentration). The freshly prepared dispersions were stored in several polypropylene tubes of (2.74 cm diameter) 50 ml volume so as to have 5 ml of empty space above the dispersion. The samples were purged with N_2 , air and CO_2 . 2.8 mass% Laponite dispersion with 5 mM NaCl was also used, and exposed this dispersion to only CO_2 environment. The reason for employing this system is discussed in the next section. All the tubes were stored in different desiccators. The free space of the desiccators was also purged with the same gas as that in the free space of tubes. For each experiment a fresh tube was used without disturbing the others. The samples were investigated for a period of 30 days with an interval time of 5 days. The time, over which the sample was kept under quiescent condition, is represented as rest time (t_r).

Changes in pH and ionic conductivity of a dispersion were measured using Horiba F-71 pH Meter and Horiba DS-71 Conductivity meter respectively. Extent of dissolution of the Laponite particle leading to leaching of Mg^{2+} ions was studied by performing complexometric titration, wherein dispersion is titrated against EDTA (ethylenediamine tetra-acetic acid) using EBT (eriochrome black-T) as the indicator. In the presence of Mg^{2+} ions the dispersion turns red or purple on addition of EBT. To maintain the pH of 10 throughout the titration process, ammonia buffer solution (ammonium chloride/ammonia) was used. As Laponite forms thixotropic gel, the viscosity/elasticity of the dispersion was first reduced by shearing it vigorously to ease the titration process. The titration's end point occurs when EDTA changes the color of the dispersion to blue, which yields concentration of leached magnesium ion (C_{Mg}). The method is sensitive enough to detect $C_{Mg} = 10^{-3}$ mM (Vogel, 1978).

The rheological study was carried out using a cup and bob geometry (bob diameter 10.004 mm with 0.407 mm gap) of Anton Paar MCR 501 rheometer. To erase history associated with the samples on a given day after preparation (rest time), pre-shearing was performed by applying large amplitude oscillatory shear of 80,000% for 10 min. Subsequent to shear-melting, dispersion was allowed to age wherein evolution of elastic modulus (G') and viscous modulus (G'') were monitored by applying small amplitude oscillatory shear of 0.1% for 3 h. The time elapsed since shear melting has been termed as waiting time or aging time (t_w). Frequency of oscillation was maintained at 0.1 Hz.

Unless otherwise mentioned, measurements of the ionic conductivity, pH, and C_{Mg} reported below are the values averaged over the entire volume of the tube. The rheological study, on the other hand, requires very small amount of sample (around 3 ml), which was collected near the free surface. For 2.8 mass% dispersion studied here, no difference was found in the results when dispersion was stored under the N_2 or air atmosphere for all the experiments. Therefore, only the results associated with the air atmosphere are reported below. All the experiments were performed at 25 °C.

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