



Research paper

Chemical stability of Laponite in aqueous media

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ARTICLE INFO

Article history:

Received 7 March 2014

Received in revised form 2 June 2014

Accepted 4 June 2014

Available online 21 June 2014

Keywords:

Laponite
Chemical stability
Ionic conductivity

ABSTRACT

In this work the stability of Laponite against dissolution in its aqueous dispersions is investigated as a function of initial pH of water before mixing Laponite, and concentration of Laponite. Dissolution of Laponite is quantified in terms of the concentration of leached magnesium in the dispersions. Interestingly the solvent pH is observed to play no role in the dissolution of Laponite in dispersion over the explored range of 3 to 10. Furthermore, contrary to the usual belief that Laponite dissolves when the pH of aqueous dispersion decreases below 9, the dissolution of the same is observed even though dispersion pH is above 10 for low concentrations of Laponite (1 and 1.7 mass%). On the other hand, for dispersions having a high concentration of Laponite (2.8 mass%) and pH in the similar range (>10) no dissolution is observed. Measurement of ionic conductivity of dispersion shows that the concentration of sodium ions in dispersion increases with the concentration of Laponite, which appears to have a role in preventing the dissolution of Laponite.

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1. Introduction

Laponite, a synthetic clay mineral, is known to have widespread applications as a rheology modifier and as a reinforcement in a variety of industries such as mining, petroleum, home and personal care, pharmaceutical, agrochemical, and paint polymer etc. The primary particle of Laponite possesses anisotropic nanometric shape that has dissimilar charge distribution. Consequently its dispersion in water shows a rich variety of phase behaviors (Jabbari-Farouji et al., 2008; Mongondry et al., 2005; Mourchid et al., 1995; Ruzicka and Zaccarelli, 2011; Shahin and Joshi, 2012; Shahin et al., 2011; Sun et al., 2012; Tudisca et al., 2012). In addition, it attracts applications as an active agent in many water based formulations (Ghadiri et al., 2013; Negrete et al., 2004; Sun et al., 2009). The dependence of physical properties of Laponite dispersion on time, particularly the observed increase in modulus and relaxation time, is reminiscent of physical aging in molecular and spin glasses (Dhavale et al., 2013; Morariu and Bercea, 2012; Schosseler et al., 2006; Shahin and Joshi, 2011). Owing to this, aqueous dispersion of Laponite is also investigated as a model soft glassy material (Bandyopadhyay et al., 2004; Bonn et al., 2002). Over the past two decades Laponite in aqueous dispersion as well as in other multi-component systems has attracted enormous attention from the academia as well as from the industry. However, Laponite is reported to have a major shortcoming related to its chemical stability. According to Thompson and Butterworth (1992), Laponite particles undergo

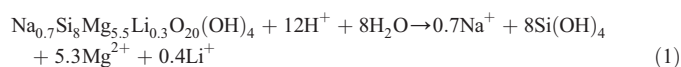
dissolution in the aqueous media having pH less than 9. Interestingly despite vast literature available on this clay mineral, very few papers study the chemical stability of Laponite dispersion, which is a subject of this work. It is observed that Laponite particles in dispersion are prone to dissolution even at high pH and the chemical stability of the same strongly depends on the concentration of Laponite.

Laponite has a chemical formula given by: $\text{Na}_{0.7}\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.3}\text{O}_{20}(\text{OH})_4$. Laponite particles are disk shaped with a thickness of 1 nm and diameter of 25 ± 2 nm (Kroon et al., 1998). In a single layer of Laponite two tetrahedral silica sheets sandwich one octahedral magnesia sheet. In the middle octahedral sheet few magnesium atoms are substituted by lithium atoms (isomorphic substitution) creating a deficiency of positive charge within the sheet. Consequently, in a dry state, the faces of Laponite particles, that are electron rich, share the electrons with sodium atoms that reside in the interlayer space. Upon dispersing in the aqueous media the Na^+ ions dissociate rendering a permanent negative charge to the faces of Laponite particles. The edge of Laponite particle predominantly contains MgOH groups from the octahedral magnesia sheets. The point of zero charge (PZC), for oxides and hydroxides of magnesium is above pH of 10 (Kosmulski, 2001). Martin et al. (2002) mentioned that according to the manufacturer (Laponite Technical Bulletin, 1990) the edge of Laponite particle, which contains predominantly MgOH, is positive below pH of 11 indicating pH of 11 to be a point of zero charge for the edges of Laponite particles. Depending upon the pH of the medium, either H^+ or OH^- ions dissociate from the edges rendering the same negative or positive charge respectively. The dissociation of H^+ ions from the edge occurs only above the pH associated with PZC to acquire the negative charge. Consequently the pH of the dispersion decreases. Below the pH associated with PZC, the edge of Laponite particle releases OH^- ions,

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which causes an increase in the pH of the dispersion. Therefore, depending upon whether H^+ or OH^- ions dissociate from the edge, the pH of dispersion respectively decreases or increases (Tawari et al., 2001), and the resultant value of the pH of Laponite dispersion has a strong influence on the stability of the same.

According to available literature, the first study on the chemical stability of hectorite in aqueous media is due to Tiller (1968). He estimated leaching of magnesium ions from naturally occurring purified hectorite using atomic absorption spectroscopy. He observed that the concentration of leached magnesium increases with the decrease in pH but remains practically independent of the concentration over the explored range of 0.1 to 0.4 mass%. The first investigation on the chemical stability of Laponite, which is a synthetic hectorite, in aqueous dispersion was performed by Thompson and Butterworth (1992). They systematically studied the effect of the pH of the medium on the stability of Laponite dispersion in the low concentration regime (below 2 mass%). They observed a detectable dissolution of Laponite below pH of 9. They proposed that such dissolution follows a chemical reaction given by:



wherein excess of H^+ ions causes leaching of magnesium ions from the particles. There is a slight difference between the formula for Laponite mentioned by Thompson and Butterworth (1992) and that adapted in this work. Thompson and Butterworth suggested the formula to be $Na_{0.8}Si_8Mg_{5.4}Li_{0.4}O_{20}(OH)_4$, while this work subscribes to the formula suggested by the manufacturer. The above reaction therefore has been stoichiometrically corrected to suit Laponite used in this study.

Mourchid and Levitz (1998) studied long term gelation of aqueous dispersion of Laponite having a low concentration of Laponite (1 and 1.5 mass%). They observed that samples preserved under inert conditions (nitrogen atmosphere in this case) do not undergo dissolution (do not show any traces of Mg^{+2} ions). On the other hand, the samples that are merely sealed indeed show presence of Mg^{+2} ions, which increases as a function of time. They report that all the samples wherein the concentration of Mg^{+2} ions is observed to be greater than 0.5 mM form viscoelastic gels. They claim that the dissolution of atmospheric CO_2 is sufficient to create an acidic environment which according to reaction (1) leads to leaching of Mg^{+2} ions. Interestingly Mourchid and Levitz (1998) prepare the dispersions of Laponite in water having pH 10. However they do not report the pH of dispersion when the presence of Mg^{+2} ions was observed. Apparently studies by Thompson and Butterworth (1992) and Mourchid and Levitz (1998) are the only two reports available in the literature on the chemical stability of Laponite dispersion. Both the reports suggest the possibility of leaching of Mg^{+2} ions when the pH of dispersion is below 9.

2. Materials and experimental procedure

Laponite XLG® used in this study is obtained from Southern Clay Products Inc. Laponite is dried for 4 h at 120 °C to remove the moisture and is subsequently mixed with Millipore water (Resistivity = 18.2 MΩ·cm) having pH in the range of 3 to 10. For maintaining the acidic pH two reagents have been used, namely: citric acid buffers as well as HCL. Citric acid buffers are prepared by incorporating 0.1 M citric acid and 0.1 M tri-sodium citrate solutions in water. In order to maintain the basic pH, NaOH has been employed. In some samples, NaCl has also been incorporated. Once the predetermined initial pH of water and salt concentration are obtained the dried Laponite powder is added to the same. Mixing is carried out using an Ultra Turrex drive for a period of 45 min. The dispersions are then stored in sealed polypropylene bottles without any nitrogen purging. After the sample preparation bottles are filled in such fashion that they have around 200 ml of open space filled with air above the sample. However, the bottles are opened in order to take out the sample for pH and Mg^{+2} ion

concentration measurements at predefined interval of days (duration between two consecutive samples vary between 1 and 5 days). The list of samples studied in this work with respect to concentrations of Laponite and initial pH is reported in Table 1. Throughout in this paper the pH of water before mixing Laponite is represented as pH_i . On the other hand, the pH of dispersion (after the addition of Laponite) is termed as pH_f which is observed to depend on time.

In order to detect the concentration of Mg^{+2} ions in Laponite dispersion, complexometric titration is performed on dispersion samples at a regular interval after the preparation of the same. Complexometric titration is performed with EDTA using eriochrome black-T as an indicator. If dispersion contains Mg^{+2} ions, it turns red or purple upon the addition of eriochrome black-T indicator. The method is so sensitive that it can detect the concentration of Mg^{+2} ions as small as 10^{-3} mM (Vogel, 1978). The details of complexometric titration procedure can be found elsewhere (Vogel, 1978). It is important to note that Laponite dispersion forms a high viscosity/elasticity gel, and therefore, in principle, the titration of the same in this form is difficult. However, Laponite gel is thixotropic, therefore its viscosity/elasticity can be reduced significantly by simply shearing it vigorously. Therefore, it has been made sure that the gel viscosity has reduced significantly by shearing it to the extent possible so that it is in liquid state at the time of titration. The changes in ionic conductivity and pH_f were also measured as a function of time using Eutech Cyberscan CON 6000 pH and conductivity meter with a 4 cell conductivity electrode (range 0–500 mS and temperature range 0–70 °C) and an open pore double reference junction Ag/AgCl pH electrode (range pH 0–14 and temperature 0–80 °C). All the experiments are performed at 25 °C.

3. Results and discussion

Upon incorporating Laponite in water the nature of resultant dispersion is strongly influenced by pH_i and reagents used to maintain the pH_i . Particularly, 2.8 mass% dispersions have been prepared in water with pH_i between 3 and 10. As mentioned before, in order to maintain acidic pH_i , two reagents namely citric acid buffer and HCl are used. It is observed that when pH_i is maintained (in the range of 3 to 10) by using either HCl or NaOH, dispersions of 2.8 mass% Laponite are transparent and eventually acquire a soft solid like consistency. On the other hand, when citric acid buffer is used to maintain pH_i of 3 and 4, resultant 2.8 mass% dispersions show sedimentation wherein Laponite settles down within a day. However, for $pH_i = 6$ (obtained by citric acid buffer) 2.8 mass% dispersion does not undergo sedimentation, but becomes hazy and remains in the liquid state throughout the observation period of 30 days. In addition, 1 and 1.7 mass% dispersions are also prepared in water having pH_i between 7 and 10. It is observed that 1 mass% dispersion remains in liquid state without noticeable change in viscosity over a period of 30 days. Dispersions having 1.7 mass% concentration also remain in liquid state but become progressively more viscous over the observation period of 30 days.

The incorporation of Laponite in water, depending upon pH_i , leads to dissociation of OH^- ions from its edge. Such dissociation in turn causes an increase in the pH_f of the dispersion. In Figs. 1 and 2 the evolution of dispersion pH_f is plotted as a function of number of days since the preparation of the same for different concentrations of Laponite. For 1 and

Table 1
List of samples studied for chemical stability against Mg^{+2} ion leaching.

Laponite conc. (mass%)	Acidic pH_i (no salt)	Neutral and basic pH_i (no salt)	Concentration of NaCl (mM) with $pH_i = 7$
1	–	$pH_i = 7, 8, 9$ and 10.	11.1
1.7	–	Basic pH_i maintained	7.2
2.8	$pH_i = 3, 4$ and 6 maintained by citric acid buffer as well as HCL	by NaOH	–

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