



Research paper

Chemical stability phase diagram of aqueous Laponite dispersions



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ABSTRACT

A synthetic clay mineral Laponite has been reported to undergo chemical degradation when dispersed in aqueous media causing magnesium ions from the same to leach out. This work systematically studies chemical degradation of Laponite particles in aqueous dispersions preserved under ambient air as a function of concentration of Laponite as well as that of externally added salt (NaCl). Along with measurement of concentration of magnesium ions using complexometric titration, pH and ionic conductivity of the dispersions are also measured at regular interval. Interestingly, for the studied dispersions, pH of a dispersion does not have any direct effect on chemical degradation of Laponite. Increase in concentration of Laponite as well as that of salt, on the other hand, is observed to have stabilizing effect against degradation. Finally a chemical stability phase diagram is proposed which indicates dispersion having higher concentrations of Laponite and salt are more stable. Conversely, with increase in time elapsed since preparation, Laponite particles in dispersion are more prone to degradation. The experimental data is analyzed to investigate mechanism of degradation and site of hydrogen ion attack on the Laponite particles.

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1. Introduction

Laponite is a synthetic hectorite manufactured by processing combined salts of sodium, magnesium and lithium along with sodium silicate (Laponite Technical Bulletin, 1990). Over past two decades Laponite has attracted attention from academic community due to its rich phase and rheological behavior (Ruzicka and Zaccarelli, 2011; Shahin and Joshi, 2012a). Moreover, Laponite is used as a rheology modifier in variety of industries such as petroleum, polymer, healthcare, personal care, home care, pharmaceutical, agrochemical, paper, textile, etc. (Laponite Technical Bulletin, 1990) and also in many water based formulations (Negrete et al., 2004; Sun et al., 2009; Ghadiri et al., 2013). While use of Laponite for academic as well as industrial applications is increasing, the system is marred by reports related to its chemical degradation when dispersed in aqueous medium under certain conditions (Thompson and Butterworth, 1992; Mouchid and Levitz, 1998; Jatav and Joshi, 2014). The objective of the present paper is to propose a chemical stability phase diagram of aqueous Laponite dispersion as a function of time for a broad range of concentrations of Laponite as well as that of externally added salt (NaCl).

Hydrous sodium lithium magnesium silicate or Laponite is a disk shaped nanoparticle with diameter around 25 ± 2 nm and thickness 0.92 nm (Kroon et al., 1996). Its unit cell has a chemical formula: $\text{Na}_{0.7}\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.3}\text{O}_{20}(\text{OH})_4$. A primary layer of Laponite is composed of octahedral magnesia sheet that is sandwiched between two tetrahedral

sheets of silica. Owing to isomorphous substitution of divalent magnesium by monovalent lithium there is a deficiency of positive charge within the Laponite layer, which is balanced by sodium atoms that reside in the interlayer space. When dispersed in aqueous media the sodium ions dissociate rendering the opposite faces of Laponite disks a permanent negative charge. The edges of Laponite disks constitute broken crystal composed of hydroxides of magnesium as well as that of silicon. The point of zero charge for MgOH is known to be pH of 12.5 while that of for SiOH is around 2 (Stumm, 1992). Consequently, below the pH of 12.5 the edges of Laponite where MgOH is located are expected to possess positive charge. However, there is a coupling between the nature of the edge charge, nature of the faces and the pH of the medium (Tawari et al., 2001; Tombácz and Szekeres, 2004). In order to render positive charge to the edge, OH^- ions must dissociate that causes increase in pH of the medium. Conversely so as to have negative charge on the edge, H^+ ions must dissociate leading to decrease in pH of the medium. Furthermore H^+ ions from the bulk get adsorbed on the negative faces of Laponite. Higher the pH is, lower would be the adsorption owing to lesser availability of H^+ ions. Such adsorption results in increase in pH of the dispersion.

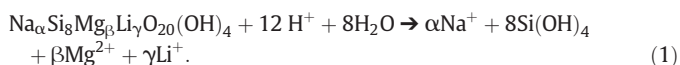
In an aqueous medium, owing to the presence of negative as well as positive charges and anisotropic structure, Laponite particles share attractive and repulsive interactions with each other (Shahin and Joshi, 2012b), which leads to a very rich phase behavior (Mouchid et al., 1995; Mongondry et al., 2005; Sun et al., 2012; Tudisca et al., 2012). It is typically observed that incorporation of Laponite in water beyond 1 mass% leads to continuous increase in viscosity and elasticity of a dispersion, eventually leading to soft solid like consistency that sustains its

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own weight against gravity. This process of increase in elasticity as well as viscosity has been termed in the literature as physical aging. Interestingly the presence of ions due to dissociation of externally added salt in the Laponite dispersion is observed to accelerate the process of physical aging (Saha et al., 2015). It is generally accepted that space spanning attractive fractal gel is responsible for such behavior for concentrations less than 2 mass% (Ruzicka and Zaccarelli, 2011). The nature of microstructural organization beyond 2 mass% is, however, a matter of debate; with one school proposing formation of a repulsive glass (Ruzicka and Zaccarelli, 2011) while the other proposing a presence of attractive gel (Mongondry et al., 2004). Nonetheless, irrespective of the microstructure, time evolution of the physical properties of Laponite dispersion is reminiscent of physical aging observed in molecular glasses. Consequently aqueous dispersion of Laponite is considered as a model soft glassy material (Angelini et al., 2014; Kaushal and Joshi, 2014).

While the dispersions of Laponite are of academic and practical significance, the particles of Laponite have been reported to be vulnerable for chemical degradation under certain conditions. Chemical stability of hectorite clay minerals has been investigated over several decades, wherein it has been proposed that H^+ ions react with hectorite leading to leaching of Mg^{2+} ions (Kerr et al., 1956; Tiller, 1968; Kreit et al., 1982). These reports suggest that H^+ ions attack hectorite at two places, the edge and the faces. On the edge both tetrahedral and octahedral layers are exposed and interaction of the same with H^+ ions is straightforward. On the contrary, on faces only the oxygen rich part of the tetrahedral silica layer is exposed. It has been proposed that H^+ ions adsorbed on the faces diffuse through the tetrahedral layer and interact with the magnesia in the octahedral layer. Kerr et al. (1956) claim that leaching of Mg^{2+} ions take place from the edges in the presence of weak acids while by diffusion of H^+ ions through tetrahedral structure in the presence of strong acids. Tiller (1968) suggested that during the initial period edges are more vulnerable for acid attack, on the other hand, Kreit et al. (1982) proposed prominence of face attack. Interestingly Kreit et al. (1982) also observed that addition of salt has a stabilizing effect against leaching of magnesia from hectorite. This effect has been attributed to increased concentration of cations associated with salt near the particle that prevent its interaction with H^+ ions.

Thompson and Butterworth (1992) were the first to study the chemical stability of Laponite dispersion. They systematically investigated effect of pH up to Laponite concentration of 2 mass%. They proposed that when pH of the aqueous media decreases below a value of 9, Laponite disintegrates according to following chemical reaction:



There is a minor difference in the unit cell chemical composition of Laponite used by Thompson and Butterworth (1992) ($\alpha = 0.8$, $\beta = 5.4$ and $\gamma = 0.4$) and the one used in the present work ($\alpha = 0.7$, $\beta = 5.5$ and $\gamma = 0.3$). Mourchid and Levitz (1998) observed that for 1 and 1.5 mass% aqueous dispersions of Laponite preserved under ambient air, the process of physical aging is significantly faster compared to when the same dispersions were preserved under nitrogen atmosphere. Such behavior was attributed to dissolution of CO_2 from ambient air, which causes decrease in pH of the same, leading to chemical degradation of Laponite according to Eq. (1) producing Mg^{2+} and Li^{+} ions.

Very recently Jatav and Joshi (2014) studied chemical stability of Laponite for three concentrations of Laponite with and without salt for different initial pH of water used for making dispersion. They preserved the dispersions under ambient air atmosphere and measured concentration of Mg^{2+} ions using complexometric titration as a function of number of days after preparing the same. They observed that initial pH of water over the range 3 to 10 has practically no effect on chemical

degradation of Laponite. This is because incorporation of Laponite raises pH of water above 10 even though the initial pH is between 3 and 10. For low concentrations (below 1 and 1.7 mass%), however, Laponite is observed to undergo chemical degradation even though the pH of a dispersion is above 10. On the other hand, for higher concentration of Laponite (2.8 mass%), no chemical degradation is observed for the same pH. Overall Jatav and Joshi (2014) reported that not just the greater concentration of salt but higher concentration of Laponite also has a stabilizing effect against chemical degradation. The present paper is a sequel of Jatav and Joshi (2014) work, wherein chemical stability of dispersion is studied over a broad range of concentrations of Laponite (1 to 4 mass%) and that of NaCl (0 to 7 mM) over a period of 40 days at regular interval (even when no salt is added externally, concentration of external Na^{+} ions in a dispersion is 0.1 mM due to NaOH added to the dispersion for maintaining pH 10). In this work, pH and ionic conductivity of dispersion are also measured in addition to concentration of leached Mg^{2+} ions if any. Based on the observations, a chemical stability phase diagram is proposed for Laponite dispersion preserved under ambient air as a function of Laponite concentration, salt concentration and rest time. Considering widespread applications of Laponite in aqueous media, such phase diagram is expected to prove useful while designing experiments and products.

2. Material and experimental procedure

Laponite XLG® (BYK Additives Ltd.) was dried for 4 h at 120 °C to remove moisture. Dried white powder of Laponite was dispersed in ultra-pure water (resistivity 18.2 MΩ-cm) having pH 10 (maintained with NaOH) and salt (NaCl) using an Ultra Turrex Drive for a period of 45 min to ensure the preparation of dispersion. The samples were stored in sealed polypropylene bottles having open space of 100 ml having ambient air. Samples necessary to carry out the tests were collected from the bottles at an interval of 5 days up to 40 days.

As shown in the next section, dissolution of CO_2 causes decrease in pH of a dispersion and leads to leaching of Mg^{2+} ions. Our calculations suggest that amount of CO_2 present in the air above the sample is significantly in excess of what is required for observed decrease in pH as well as to cause leaching of Mg^{2+} ions over 40 days. On the other hand, though we 'seal' the bottle, it is opened for taking out the sample to measure pH and Mg^{2+} ion concentration at predetermined interval of days. Consequently, air above the sample gets renewed each time. Furthermore, amount of air present in the bottle also increases as more and more sample is taken out. Consequently for all the practical purposes the present system can be considered to be an open system as availability of CO_2 in air is not a controlling step.

Chemical degradation of Laponite particle was quantified by measuring concentration of leached Mg^{2+} by performing complexometric titration of the sample with ethylene diamine tetra-acetic acid (EDTA) using eriochrome black-T (EBT) as an indicator. This process is based on the formation of Mg^{2+} -eriochrome black-T complex which changes the color of dispersion to red or purple. Magnesium free samples do not undergo any color change. Since the sample tends to form high viscosity gel, in order to facilitate the titration process, viscosity of the sample was reduced by shearing it vigorously. Complexometric titration is sensitive to the concentration of Mg^{2+} ions as small as 10^{-3} mM. Details of the complexometric titration process can be found elsewhere (Vogel, 1978). Ionic conductivity and pH of dispersions are also measured 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) with an open pore double reference junction Ag/AgCl pH electrode (range pH 0–14 and temperature 0–80 °C). Since in an aged Laponite dispersion ionic mobility is known to be constrained (Dhaval et al., 2013), before measuring the conductivity and the pH, a dispersion is shear melted so as to facilitate unhindered ionic mobility. In this work for all the experiments temperature of 25 °C is maintained.

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