



Research paper

# Chemical stability of Laponite in aqueous media

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## 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

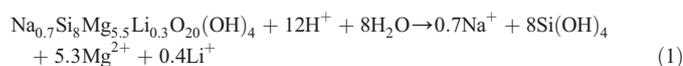
dissolution in the aqueous media having pH less than 9. Interestingly despite vast literature available on this clay mineral, very few papers study the chemical stability of Laponite dispersion, which is a subject of this work. It is observed that Laponite particles in dispersion are prone to dissolution 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  $25 \pm 2$  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  $\text{Na}^+$  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  $\text{H}^+$  or  $\text{OH}^-$  ions dissociate from the edges rendering the same negative or positive charge respectively. The dissociation of  $\text{H}^+$  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  $\text{OH}^-$  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.

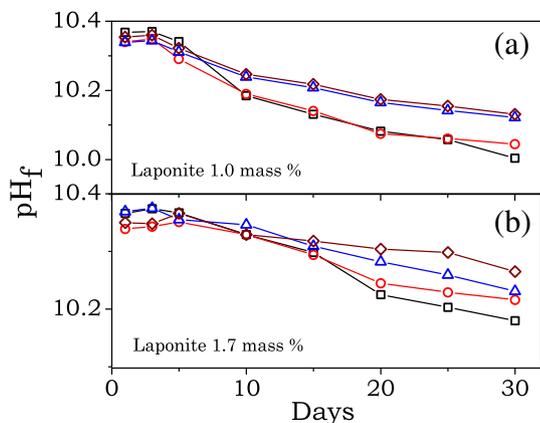
## 3. Results and discussion

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.

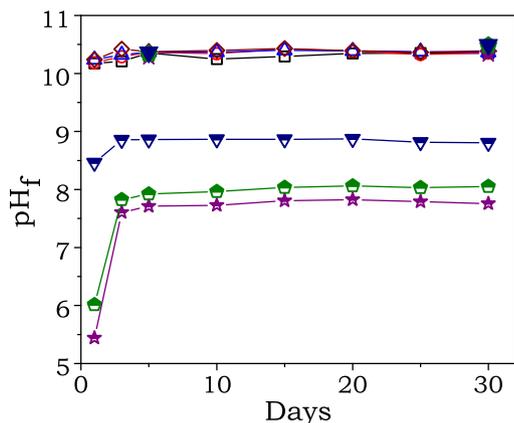
Laponite conc. (mass%)	Acidic $pH_i$ (no salt)	Neutral and basic $pH_i$ (no salt)	Concentration of NaCl (mM) with $pH_i = 7$
1	–	$pH_i = 7, 8, 9$ and 10.	11.1
1.7	–	Basic $pH_i$ maintained	7.2
2.8	$pH_i = 3, 4$ and 6 maintained by citric acid buffer as well as HCL	by NaOH	–



**Fig. 1.** Evolution of  $pH_f$  of (a) 1 mass% and (b) 1.7 mass% Laponite dispersions plotted as a function of number of days after preparing the same in water having  $pH_i = 7$  (squares), 8 (circles), 9 (up triangles) and 10 (diamonds). The lines serve as a guide to the eye.

1.7 mass% Laponite dispersions with  $pH_i$  in the range of 7 to 10, the time dependent evolution of  $pH_f$  is shown in Fig. 1a and b respectively. It can be seen that soon after mixing Laponite,  $pH_f$  increases to values above 10. As time passes,  $pH_f$  decreases weakly as a function of time, so that over a period of 30 days  $pH_f$  still remains above 10. Furthermore, a lesser decrease in  $pH_f$  is observed in dispersions prepared in water with greater  $pH_i$ .

Variation in  $pH_f$  for 2.8 mass% Laponite dispersion for  $pH_i$  in the range of 3 to 10 is shown in Fig. 2. For 2.8 mass% Laponite dispersion with acidic  $pH_i$  (3 to 6) maintained by citric acid buffer,  $pH_f$  increases within the first 5 days and then remains constant. The value of constant  $pH_f$  always remains below 9. On the other hand, if the acidic  $pH_i$  (3 to 6) is maintained by HCl, the addition of 2.8 mass% Laponite causes an increase in  $pH_f$ , which also stabilizes within the first 5 days and remains nearly constant at a value of 10.4 irrespective of the value of  $pH_i$ . For 2.8 mass% dispersions with  $pH_i$  in the range of 7 to 10 (basic  $pH_i$  maintained by NaOH) the increase in their  $pH_f$  values are also observed. However regardless of  $pH_i$ ,  $pH_f$  is observed to reach a constant level of around 10.4 after 5 days. Interestingly for 2.8 mass% Laponite dispersion having  $pH_f$  in the range of 3 to 10 maintained by either HCl or NaOH,  $pH_f$  after 5 days is observed to be very similar and around 10.4. It should be noted that below a point of zero charge (PZC), which is around pH of 11 for the edge of Laponite particle (Martin et al., 2002),



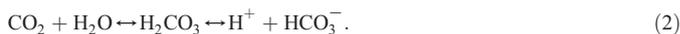
**Fig. 2.** Evolution of  $pH_f$  of 2.8 wt.% Laponite dispersion plotted as a function of number of days after preparing the same in citric acid buffer solution (half filled symbols) having  $pH_i = 3$  (stars), 4 (pentagons), and 6 (down triangles); in HCl solution (filled symbols) having  $pH_i = 3$  (stars), 4 (pentagons), and 6 (down triangles); and in NaOH solution (open symbols) having  $pH_i = 7$  (squares), 8 (circles), 9 (up triangles) and 10 (diamonds). The lines serve as a guide to the eye.

edges acquire a positive charge by dissociating  $OH^-$  ions. Such dissociation of  $OH^-$  ions raises the pH of the aqueous media in which Laponite particles are dispersed in. Since the dissociation of  $OH^-$  ions from the edges of Laponite particle depends upon the pH of the surrounding aqueous medium and not the initial pH, at pH of 10.4 the dissociation from the edge stops and pH does not increase any further.

In Fig. 3, the comparison of the results of Figs. 1 and 2 are shown, wherein  $pH_f$  on day 5 was plotted as a function of  $pH_i$ . It can be seen that dispersions prepared in citric acid buffer show a qualitatively different behavior than the rest of the dispersions. This different behavior can be understood as follows. In aqueous solution, the incorporation of an incremental amount of acid or base (or a compound that tends to release  $OH^-$  or  $H^+$  ions) tends to change its  $pH_f$  gradually. In a buffer, on the other hand, a mixture of weak acid (in this case citric acid) and its conjugate base (in the present case tri-sodium citrate) is used, which causes only a small change in  $pH_f$  even when a strong acid or base is incorporated in the same. Buffer solutions tend to resist change in  $pH_f$  owing to the equilibrium between acid and its conjugate base (Bettelheim et al., 2009). This aspect is very evident from Fig. 2. Consequently the  $pH_f$  of Laponite dispersion prepared in citric buffer always remains below 9.

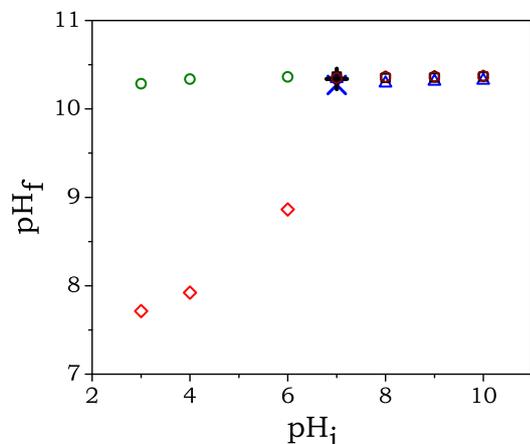
The change in  $pH_i$  upon the incorporation of Laponite in water has an important consequence as the resultant  $pH_f$  of Laponite dispersion, as reported in the literature, is proposed to affect the chemical stability of the Laponite particles in the dispersion. As discussed before, in the presence of  $H^+$  ions, Laponite particles undergo reaction (1), which results in leaching of magnesium ( $Mg^{+2}$ ) and lithium ( $Li^+$ ) ions. In this work, the estimation of the concentration of  $Mg^{+2}$  ions is carried out by the complexometric titration of Laponite dispersions at regular intervals. The corresponding measured concentration of  $Mg^{+2}$  ions for three concentrations of Laponite as a function of number of days since the preparation of the same is plotted in Fig. 4. Laponite dispersions having 2.8 mass% concentration with acidic  $pH_i$  obtained by citric acid buffer (and  $pH_f < 9$  for all samples) shows a significant amount of leaching of  $Mg^{+2}$  ions, whose magnitude also increases with time as shown in Fig. 4a. For dispersions having, concentrations 1 and 1.7 mass% and  $pH_i = 7$  to 10 (and  $pH_f > 10$  for all samples) also shows the measurable presence of  $Mg^{+2}$  ions at very early age, which increases with time. Interestingly the magnitude of  $Mg^{+2}$  ions present in 2.8 mass% dispersion with  $pH_i$  maintained by citric acid buffer is observed to be significantly greater in magnitude than lower concentration dispersions whose  $pH_i$  is maintained by NaOH. However, most surprisingly, for 2.8 mass% Laponite dispersion with  $pH_i = 3$  to 10 maintained by adding HCl or NaOH, no traces of  $Mg^{+2}$  ions are observed over the explored duration of 30 days.

As mentioned in the Introduction section, the very first report on the chemical stability of Laponite by Thompson and Butterworth (1992) claims that particles of Laponite undergo dissolution leading to leaching of  $Mg^{+2}$  ions when  $pH_f$  decreases below 9. However the present study clearly demonstrates that even though the  $pH_f$  is above 10, leaching of  $Mg^{+2}$  ions does take place in the dispersions having a low Laponite concentration. Surprisingly the dispersions with 2.8 mass% concentration, although has  $pH_f$  in the similar range as that of the low concentration dispersions, do not show any measurable presence of  $Mg^{+2}$  ions. Even though the overall  $pH_f$  is basic, as suggested by Mouchid and Levitz (1998), the dissolution of atmospheric  $CO_2$  in water produces carbonic acid and hence  $H^+$  ions locally according to (Greenwood and Earnshaw, 1997):



Therefore continuous enhancement of  $Mg^{+2}$  ions reported in Fig. 4 can be attributed to the slow dissolution of  $CO_2$  from the atmosphere that follows reactions (1) and (2).

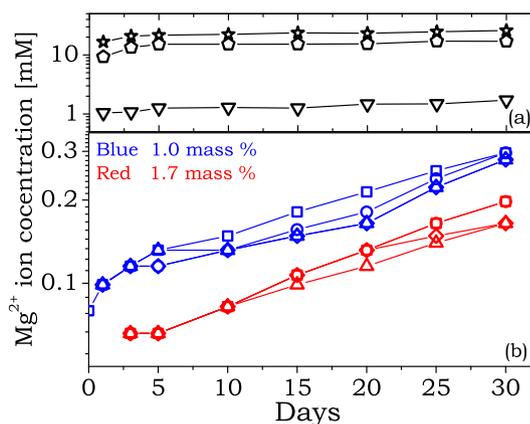
The reason of this significant leaching of  $Mg^{+2}$  ions in 2.8 mass% Laponite dispersion ( $pH_i$  controlled by citric acid buffer) is the already



**Fig. 3.**  $\text{pH}_f$  of dispersion on day 5 is plotted as a function of  $\text{pH}_i$  at different concentrations: 1 mass% (up triangles: no salt, multiplication sign ( $\times$ ): 11.1 mM NaCl), 1.7 mass% (squares: no salt, plus sign (+): 7.2 mM NaCl), 2.8 mass% with  $\text{pH}_i$  maintained by HCl or NaOH (circles) and citric acid buffers (diamonds).

low  $\text{pH}_f$  of dispersion compared to all the other dispersion samples aided by the dissolution of atmospheric  $\text{CO}_2$ . The dissolution of Laponite in low concentration dispersion with  $\text{pH}_i$  in the range of 7 to 10 and  $\text{pH}_f \approx 10.4$  can be ascribed to the dissolution of atmospheric  $\text{CO}_2$ , which leads to the generation of  $\text{H}^+$  ions locally. As soon as  $\text{H}^+$  ions are generated, there is competition between Laponite particles and  $\text{OH}^-$  ions (associated with the basic environment). If  $\text{H}^+$  ions react with Laponite it will lead to dissolution. On the other hand, if  $\text{H}^+$  ions react with  $\text{OH}^-$  ions, it will cause a decrease in pH. (In this work, as mentioned in Table 1, 1 and 1.7 mass% dispersions in water having acidic  $\text{pH}_i$  are not studied. Since even 1 and 1.7 mass% dispersions prepared in basic  $\text{pH}_i$  demonstrate leaching of  $\text{Mg}^{2+}$  ions, it is obvious that 1 and 1.7 mass% dispersions in water having acidic  $\text{pH}_i$  will also show the dissolution of Laponite particles.) The stability of 2.8 mass% Laponite dispersion where  $\text{pH}_i$  is controlled by HCl or NaOH (with  $\text{pH}_i = 3$  to 10 and  $\text{pH}_f \approx 10.4$ ) observed in the third case is however puzzling.

It is known that  $\text{CO}_2$  has a significant affinity toward NaOH, and dissolved  $\text{CO}_2$  reacts with NaOH to first form sodium bicarbonate ( $\text{CO}_2 + \text{NaOH} \rightarrow \text{NaHCO}_3$ ) and finally sodium carbonate ( $\text{NaHCO}_3 + \text{NaOH} \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$ ). Therefore greater concentration of NaOH in solution/dispersion is expected to inhibit the formation of carbonic acid and  $\text{H}^+$  ions, and in turn prevents leaching of the  $\text{Mg}^{2+}$  ions. However, for 1, 1.7 and 2.8 mass% dispersions (with  $\text{pH}_i$  maintained either by HCl or NaOH), the  $\text{pH}_f$  is always around 10.4 over the explored



**Fig. 4.** Concentration of  $\text{Mg}^{2+}$  ions in Laponite dispersion plotted as a function of days elapsed since the preparation of dispersion for (a) 2.8 mass% dispersion with  $\text{pH}_i$  maintained by citric acid buffers, and (b) 1.0 and 1.7 mass% dispersions. The symbols represent, star:  $\text{pH}_i = 3$ , pentagon:  $\text{pH}_i = 4$ , down triangle:  $\text{pH}_i = 6$ , square:  $\text{pH}_i = 7$ , circle:  $\text{pH}_i = 8$ , up triangle:  $\text{pH}_i = 9$  and diamond:  $\text{pH}_i = 10$ . The lines serve as a guide to the eye.

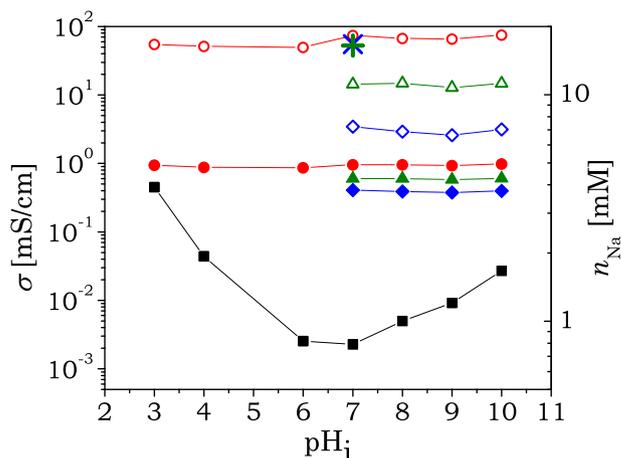
period as shown in Figs. 1 to 3. Consequently the concentration of solvated NaOH is also the same in all these cases. This suggests that effects originating from a higher concentration of Laponite are able to prevent the reaction of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  that produces  $\text{H}^+$  ions.

In order to investigate the effect of Laponite concentration further, the ionic conductivity measurements of 1 and 1.7 mass% Laponite dispersions ( $\text{pH}_i = 7$  to 10 maintained by NaOH) and 2.8 mass% Laponite dispersion ( $\text{pH}_i = 3$  to 10 maintained by HCl or NaOH) are also carried out. In Fig. 5 ionic conductivity ( $\sigma$ ) as a function of  $\text{pH}_i$  is plotted (filled symbols) for different concentrations of Laponite. The reported conductivity is measured on day 5 after preparing the dispersion. It can be seen that the ionic conductivity of solvent as a function of  $\text{pH}_i$  shows a minimum at 7. The corresponding ionic conductivity of Laponite dispersion, however, seems to be independent of  $\text{pH}_i$  over the explored range but shows greater increase for a higher concentration of Laponite. The reason behind enhancement in the conductivity of water having certain  $\text{pH}_i$  after the addition of Laponite is primarily due to the dissociation of  $\text{Na}^+$  counterions from the faces of the Laponite particles. Furthermore as shown in Fig. 3, the incorporation of Laponite in water having different  $\text{pH}_i$  causes an increase in the  $\text{pH}_f$  of the dispersion suggesting the dissociation of  $\text{OH}^-$  counterions. Such dissociated  $\text{OH}^-$  counterions from the edges are also responsible for the increase in ionic conductivity shown in Fig. 5.

The ionic conductivity ( $\sigma$ ) of a solution/dispersion is related to the concentration of  $i$ th type of ion ( $n_i$ ) present in the same by (Benenson et al., 2002):

$$\sigma = e \sum_i \mu_i n_i \quad (3)$$

where  $\mu_i$  is the mobility of  $i$ th type of ion and  $e$  is the electron charge. The dispersion of Laponite primarily contains  $\text{Na}^+$ ,  $\text{OH}^-$ ,  $\text{H}^+$  and  $\text{Cl}^-$  ions, wherever applicable, that contributes to the ionic conductivity. However at the dispersion  $\text{pH}_f$  of around 10.4, the concentration of  $\text{H}^+$  ions is very small to influence the conductivity. It is important to note that, leaching of  $\text{Mg}^{2+}$  and  $\text{Li}^+$  ions in 1 and 1.7 mass% dispersions has a very little effect on the ionic conductivity because of their small concentration compared to the other ions. Therefore, their effect is neglected in these calculations. The concentration of  $\text{OH}^-$  ion can be directly obtained from the  $\text{pH}_f$  of dispersion as  $n_{\text{OH}^-} = 10^{\text{pH}_f - 14}$ . The  $\text{Cl}^-$  ions are present only for those dispersions that are prepared in water having acidic  $\text{pH}_i$ . Therefore the concentration of  $\text{Cl}^-$  ions is given by:  $n_{\text{Cl}^-} = 10^{-\text{pH}_i}$  (for  $\text{pH}_i < 7$ ). The knowledge of mobilities of the mentioned ions ( $\mu_{\text{Na}^+} = 5.19 \times 10^{-8} \text{ m}^2/\text{sV}$ ,  $\mu_{\text{Cl}^-} = 7.908 \times 10^{-8} \text{ m}^2/\text{sV}$  and



**Fig. 5.** Ionic conductivity,  $\sigma$  (filled symbol) and sodium ion concentration,  $n_{\text{Na}}$  (open symbols) are plotted as a function of  $\text{pH}_i$  (maintained either by HCl or NaOH) after 5 days of preparation of dispersion for 1 (diamond: no salt, multiplication sign ( $\times$ ): 11.1 mM NaCl), 1.7 (up triangle: no salt, plus sign (+): 7.2 mM NaCl), 2.8 (circle) mass% Laponite dispersion and solvent conductivity (squares). The lines serve as a guide to the eye.

$\mu_{OH} = 2.05 \times 10^{-7} \text{ m}^2/\text{sV}$  (Haynes, 2010) and conductivity ( $\sigma$ ), therefore directly leads to the estimation of the concentration of  $\text{Na}^+$  ions in the dispersion.

In Fig. 5,  $n_{\text{Na}}$  has been plotted for the studied dispersions, wherein the concentration of  $\text{Na}^+$  ions can be seen to be increasing with the increase in the concentration of dispersion, but is independent of  $\text{pH}_i$  irrespective of whether it is acidic or basic if maintained either by HCl or NaOH. The concentration of  $\text{Na}^+$  ions in 2.8 mass% dispersion is almost double than that of at 1.7 mass% dispersion, though at both the concentration dispersions have similar  $\text{pH}_f$ . This result indicates that greater  $n_{\text{Na}}$  might be having a stabilizing effect on Laponite dispersion against  $\text{CO}_2$  dissolution. In order to test this hypothesis further, two dispersions are prepared, which are 1 and 1.7 mass% Laponite in water having  $\text{pH}_i = 7$  with 11.1 and 7.2 mM NaCl, respectively. The concentration of NaCl is decided in such a fashion that  $n_{\text{Na}}$  in 1 and 1.7 mass% dispersions matches with that of 2.8 mass% dispersion. The corresponding  $\text{pH}_f$  and  $n_{\text{Na}}$  for these two dispersions having NaCl are plotted in Figs. 3 and 5 respectively, which can be seen to be closely matching with that of 2.8 mass% dispersion. The concentration of  $\text{Mg}^{+2}$  ions is measured in both these dispersions (1 and 1.7 mass% having salt), and remarkably both the dispersions are observed to be free of any measurable amount of  $\text{Mg}^{+2}$  ions. This experiment clearly indicates a possible key role played by  $\text{Na}^+$  ion concentration in stabilizing Laponite dispersion against dissolution. It should be noted that significant amount of  $\text{Na}^+$  ions are also present in citric acid buffer. However, if the  $\text{pH}_f$  of Laponite dispersion is itself lesser than 9, the dissolution of Laponite cannot be avoided irrespective of the concentration of  $\text{Na}^+$  ions. Therefore, in citric acid buffer dispersions high concentration of  $\text{Na}^+$  ions cannot prevent the dissolution of Laponite particles.

Interestingly the observations of the present work share some similarities with that of the experiments by Thompson and Butterworth (1992), who observe the  $\text{pH}_f$  of Laponite dispersion and  $n_{\text{Na}}$  to increase simultaneously with the increase in the concentration of Laponite. They do not observe a detectable concentration of  $\text{Mg}^{+2}$  ions in dispersion having  $n_{\text{Na}} > 0.7 \text{ mM}$  and  $\text{pH}_f > 9$ . However, owing to the simultaneous increase in  $\text{pH}_f$  and  $n_{\text{Na}}$ , it is difficult to separate the independent influence of the either in the work of Thompson and Butterworth (1992). In the present study, on the other hand, leaching of  $\text{Mg}^{+2}$  ions is observed when the concentration of  $\text{Na}^+$  ions is low, but  $\text{pH}_f$  is almost identical and above 10. Therefore, the proposal of greater concentration of  $\text{Na}^+$  ions having a stabilizing effect on Laponite against dissolution is in qualitative agreement with that of Thompson and Butterworth (1992). However, Thompson and Butterworth (1992) also reported that the concentration of NaCl has practically no effect on the dissolution of Laponite dispersion; in the present work, instead, it is observed that the incorporation of NaCl in Laponite dispersion shows a further stabilizing effect. The reasons of discrepancy might be due to the differences in the procedures to manufacture Laponite dispersions used by Thompson and Butterworth (1992) and used in the present study. This is evident from that fact that Laponite used by Thompson and Butterworth (1992) has a diameter of 20 nm and thickness in the range of 2 to 4 nm, while the present Laponite has a diameter of 25 nm and thickness of 1 nm. In addition, there is also difference in the procedure employed to estimate pH and concentration of  $\text{Mg}^{+2}$  ions. In the present work the dispersion itself is tested for the pH measurement as well as for the titration to estimate the concentration of  $\text{Mg}^{+2}$  ions. Thompson and Butterworth (1992), on the other hand, perform dialysis and carry out titration and pH measurement on dialysate solution. Overall, the present work clearly indicates that in order to prevent the dissolution of Laponite particles in aqueous media, the  $\text{pH}_f$  of the dispersion is not the only criterion, but the concentration of  $\text{Na}^+$  ions also plays an important role.

#### 4. Conclusion

In this work the stability of Laponite in an aqueous dispersion against dissolution is investigated which results in leaching of magnesium ions.

For this, different aqueous dispersions are studied having different concentrations of Laponite (1, 1.7 and 2.8 mass%), different initial  $\text{pH}_i$  of water before mixing Laponite (from pH 3 to 10), and different reagents to maintain initial  $\text{pH}_i$  of water (citric acid buffer, HCl, and NaOH). When acidic  $\text{pH}_i$  of water is maintained by citric acid buffer in the range of 3 to 6, the incorporation of 2.8 mass% Laponite in the same is observed to raise the  $\text{pH}_f$  of the dispersions in between 7.5 and 9. For such dispersions, a significant amount of magnesium leaching is observed. On the other hand, when HCl or NaOH is used to maintain the  $\text{pH}_i$  of water before mixing in the range of 3 to 10, the incorporation of Laponite in the same raises its  $\text{pH}_f$  above 10 irrespective of the concentration of Laponite or the  $\text{pH}_i$  of water. Such enhancement is attributed to the dissociation of  $\text{OH}^-$  ions from the edges of the Laponite particles.

However, very importantly, although the  $\text{pH}_f$  of dispersion is above 10, leaching of magnesium ions is observed in low concentration dispersion (1 and 1.7 mass%) but not in high concentration dispersion (2.8 mass%). This observation is contrary to the usual belief that leaching of magnesium ions is possible only when the  $\text{pH}_f$  of dispersion is below 9. In order to investigate this intriguing behavior, the ionic conductivity of the dispersion is measured. Knowledge of the mobilities of various ions leads to the concentration of  $\text{Na}^+$  ions in the dispersion. It is observed that the concentration of  $\text{Na}^+$  ions in the dispersion increases with the increase in the concentration of Laponite but it is independent of the  $\text{pH}_i$  of water. Interestingly the incorporation of salt (NaCl) in 1 and 1.7 mass% dispersions, wherein the resultant concentration of  $\text{Na}^+$  ions is the same as that of 2.8 mass% dispersion, is also observed to prevent dissolution. Therefore, there is a possibility that greater concentration of  $\text{Na}^+$  ions might have a role in rendering greater stability to the Laponite dispersions against dissolution.

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