



Change of the point of zero net proton charge (pH_{PZNPC}) of clay minerals with ionic strength

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ABSTRACT

In a system where protons and hydroxide ions are the only aqueous species, the point of zero net proton charge (pH_{PZNPC}) of a mineral defines the pH at which the positively and negatively charged functional groups on its surface are equal (Drever, 1997). Ascertaining the pH_{PZNPC} of clay minerals, a ubiquitous component in soils, sediment and rivers, is useful in predicting its electrostatic interactions with charged aqueous species, colloids, and bacteria. While the pH_{PZNPC} values of most clays have been reported, the variation of pH_{PZNPC} with changing solution ionic strength (IS) and the mathematic relationship between them are not well-understood but critical in assessing the surface reactivity of clays in aqueous solutions ranging from freshwater to brines. To address this gap, we studied the relationship of the pH_{PZNPC} of three clay minerals (kaolinite, illite, and montmorillonite) at seven ionic strengths (from 0.001 to 0.1 M). Titration data for each clay were used to calculate the pH_{PZNPC} by two methods previously documented in literature: (1) using the difference between the blank titration and clay titrations, and (2) by the difference between the number of protons added during titration and the number of protons remaining in solution. The results show that: (1) unlike simple metal oxides (e.g., hematite, gibbsite, quartz), titration curves of clay minerals at different IS do not intersect at a common pH_{PZNPC} value; (2) the pH_{PZNPC} for kaolinite is around 5.6 to 6.6 while the pH_{PZNPC} for illite and montmorillonite is in the range of 9 to 10; (3) the pH_{PZNPC} value decreases systematically with increasing IS for all three clay minerals studied; and (4) the change of pH_{PZNPC} is linear with $\log(\text{IS})$. A third method using surface complexation modeling (SCM) approach was applied to calculate the pH_{PZNPC} of the clay minerals, and the results match well with Method 2. Our results allow for a more accurate estimation of clay surface charge property in aqueous environment, which, in turn, will improve model predictions of the adsorption of charged species in systems in which ionic strength changes.

1. Introduction

Over the past decade, our understanding of the mechanisms underpinning the adsorption of ions to geologic media has considerably improved through the use of sorption isotherms and experimentally-derived surface complexation modeling (e.g., Borrok and Fein, 2005; Alessi and Fein, 2010; Wang et al., 2010; Komárek et al., 2015; Liu et al., 2015; Alam et al., 2018; Liu et al., 2018;). Adsorption is generally governed by two parameters: the surface charge properties of the adsorbent and the chemical complexation of aqueous adsorbates onto specific surface functional groups (Dzombak and Morel, 1990). The point of zero net proton charge (pH_{PZNPC}) is one parameter used to assess the surface charge; by definition, it is the pH at which the surface proton charge of a mineral is zero (Drever, 1997).

The pH_{PZNPC} is often calculated using potentiometric acid-base titration data (Zhao et al., 2011; Ahmady-Asbchin and Jafari, 2012; Lützenkirchen et al., 2012a), although it has been argued that what is actually measured is the apparent net proton charge because the initial protonation condition of the surface at the start of the titration is unknown (Sposito, 1998; Hou and Song, 2004). Using this approach, titrations of the adsorbent of interest are conducted at several ionic strength values (IS), and the common intersection point (CIP) of the titration curves is assumed to be the pH_{PZNPC} (Kraepiel et al., 1998; Appel et al., 2003; Lützenkirchen et al., 2012a). It has been shown that for minerals without structural charge (e.g., metal oxides) that a CIP exists, but for those with structural charge (e.g. clay minerals) there is no CIP (Kraepiel et al., 1998; Zarzycki and Thomas, 2006; Rozalén et al., 2009; Lützenkirchen et al., 2012b). The veracity of this argument

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has been demonstrated by several previous experimental studies. For instance, Avena and Pauli (1998) titrated Na-montmorillonite at three IS values (0.006 M, 0.014 M, and 0.088 M) and the resulting titration curves were essentially parallel to one another (Avena and Pauli, 1998); Consistent with this, titration curves for both Na-montmorillonite and Na-kaolinite at ionic strength values of 0.01 M, 0.1 M and 1.0 M also failed to intersect (Tombácz et al., 2004; Tombácz and Szekeres, 2006); while simple oxides minerals, such as ferrihydrite, hematite, and goethite, all have the CIP for titrations conducted at different IS values (Dyer et al., 2003; Peacock and Sherman, 2004a).

Nonetheless, despite the existence of these previous studies, the underlying reason and mathematic relationship between ionic strength and pH_{PZNPC} have not been addressed. Moreover, debate remains as to whether a CIP exists for minerals having structural charges. For example, several studies on kaolinite and montmorillonite have found that a CIP does exist for titration curves measured at different IS values (Helmy et al., 1994; Kriaa et al., 2007; Kriaa et al., 2008; Jgambemi et al., 2009), and a theoretical derivation also proves that a CIP can exist for minerals with structural charge (Hou and Song, 2004). If there is CIP for minerals with structural charge, then the pH_{PZNPC} of clay minerals is constant and independent of IS. However, if a CIP does not exist, determination of clay pH_{PZNPC} values must be determined using another method and the pH_{PZNPC} is variable with IS.

Resolving the above discrepancy is important, because it influences the way in which we study the surface charge of minerals, and thus it directly impacts the predictive accuracy of clay surface properties in systems that have varying IS. Accordingly, this study performed acid-base titrations on three common clay minerals (kaolinite, illite, and montmorillonite) at seven IS values. Kaolinite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$ results from bonding of a silica tetrahedron to an aluminum/magnesium octahedron to form what is known as a 1:1 type (TO type) of clay mineral. The 1:1 clays are then constructed via hydrogen bonding between the O atoms of the tetrahedron of one layer with the OH groups of the octahedron of a different layer. Both montmorillonite $[(\text{Na},\text{Ca})_{0.33}(\text{Al},\text{Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2\cdot n\text{H}_2\text{O}]$ and illite $[(\text{Al}_2)(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{OH})_2\cdot \text{K}_{1-x}]$ are 2:1 type clays (TOT type), in which the octahedron is situated between two tetrahedra. Given that the outer tetrahedron of one layer faces the tetrahedron of another layer, the natural repulsive forces of the outer O atoms require interlayer cations to bridge the layers together. Importantly, all three clay minerals have structural charges resulting from the isomorphic substitution of higher valence cations by lower valence cations (Hower and Mowatt, 1966; Chiou and Rutherford, 1997; Schroth and Sposito, 1997) and the SSA, CEC and Ca/Na data can be referred to SI Table 1.

2. Materials and experimental procedures

Samples of kaolinite (KGa-2), montmorillonite (SWy-2), and illite (IMt-2) were obtained from the Clay Mineral Society, Source Clays Repository (Purdue University, West Lafayette, USA). All clays were grounded to pass a 100-mesh sieve. They were then washed three times by suspending 0.5 g of clay in 50 mL of 0.1 M sodium nitrate solution (ACS certified, Fisher Scientific) for 3 h and then centrifuged at 10,000g for 20 min. After washing, clays were frozen to -20°C for 12 h and then freeze dried.

Potentiometric titrations of clay minerals were conducted using an automated continuous titrator (Metrohm Titrand 905). Before each titration, the pH electrode was calibrated using commercial pH buffers (Thermo Fisher Scientific; pH 4.0, 7.0, 10.0). For each titration, 0.05 g of clay was suspended into 50 mL of NaNO_3 solution (concentration from 0.001 M to 0.1 M), and the suspension was then bubbled for 30 min with $\text{N}_2(\text{g})$ to ensure the solution was devoid of CO_2 . During titrations, the experimental apparatus remained sealed and was continuously bubbled with N_2 to prevent CO_2 from entering the system.

Seven concentrations of NaNO_3 electrolyte solution (0.001 M, 0.005 M, 0.01 M, 0.025 M, 0.05 M, 0.075 M, and 0.1 M) were used for

the titrations, and each clay was titrated in triplicate at each IS. A previous study showed that clays may partially dissolve at $\text{pH} < 4$ (Bibi et al., 2014); accordingly, all clays were titrated over a pH range of 4 to 10.5. Initially, a small volume of 0.1 M nitric acid (HNO_3 , ACS certified, Fisher Scientific) was added to bring pH to 4, and then 0.1 M sodium hydroxide (NaOH , ACS certified, Fisher Scientific) solution was incrementally added to bring the pH up to 10.5. The volume of acid and base added, and corresponding pH changes, were recorded at each titration step. The pH was considered stable and recorded only after an electrode stability of 12 mV/min was achieved. A blank titration, without addition of clay minerals, was performed for electrolyte solutions at each of the seven IS considered.

3. Data treatment

If a CIP does not exist for acid-base titrations of clay minerals conducted at various IS values, the pH_{PZNPC} must be calculated from titration data by determining the pH condition at which the net surface proton charge is equal to zero (Tschapek et al., 1974; Drever, 1997). This condition can be calculated using the following equation:

$$\delta_p = F * (\Gamma_{\text{H}^+} - \Gamma_{\text{OH}^-}) \quad (1)$$

where, F is faraday constant, Γ_{H^+} is the surface concentration of H^+ , and Γ_{OH^-} is the surface concentration of OH^- . It should be noted that the surface proton charges calculated are actually “apparent” charges because the impact of structural charge is not explicitly established. Two calculation methods have been previously described in the literature to determine $(\Gamma_{\text{H}^+} - \Gamma_{\text{OH}^-})$.

3.1. Method 1

The proton budget in a titration system is comprised of proton consumption at the solid surface and water hydrolysis. In a system where no mineral exists, the titration (blank titration) represents the proton budget of the hydrolysis of water. Thus, the difference between the amount of base and acid added to solid suspension (electrolyte + clay) and to a blank solution (only electrolyte) is used to determine the net consumption of H^+ by surfaces (Tschapek et al., 1974; Yates and Healy, 1980; Schroth and Sposito, 1997; Gu and Evans, 2008; Lützenkirchen et al., 2012a). With this, Eq. (1) can be expanded to:

$$\begin{aligned} \delta_p &= F * (\Gamma_{\text{H}^+} - \Gamma_{\text{OH}^-}) = \frac{F}{A} * \left(n(\text{H}^+)_{\text{ads}} - n(\text{OH}^-)_{\text{ads}} \right) \\ &= \left(\frac{F}{s * \gamma_m} \right) * (c(\text{H}^+)_{\text{ads}} - c(\text{OH}^-)_{\text{ads}}) = \left(\frac{F * V}{s * m} \right) * (c(\text{H}^+)_{\text{ads}} - c(\text{OH}^-)_{\text{ads}}) \end{aligned} \quad (2)$$

where, A is the surface area, s is the specific surface area of the solid, γ_m is the mass concentration of the solid, m is the mass of the solid, V is the volume of solution, and $c(\text{H}^+)_{\text{ads}}$ and $c(\text{OH}^-)_{\text{ads}}$ are concentrations of adsorbed H^+ and OH^- ions, respectively. $c(\text{H}^+)_{\text{ads}}$ and $c(\text{OH}^-)_{\text{ads}}$ are related to differences between the blank (b) and clay dispersion titration (d) (Lützenkirchen et al., 2012a):

$$\begin{aligned} \delta_p &= \left(\frac{F * V}{s * m} \right) * [(c(\text{H}^+)_{\text{d}} - c(\text{H}^+)_{\text{b}}) - (c(\text{OH}^-)_{\text{d}} - c(\text{OH}^-)_{\text{b}})] \text{ or } \delta_p \\ &= \left(\frac{F * V}{s * m} \right) * [(c(\text{H}^+)_{\text{d}} - c(\text{OH}^-)_{\text{d}}) - (c(\text{H}^+)_{\text{b}} - c(\text{OH}^-)_{\text{b}})] \\ &= \frac{F * V * \Delta c_{\text{d}}}{s * m} - \frac{F * V * \Delta c_{\text{b}}}{s * m} \end{aligned} \quad (3)$$

where, Δc_{d} is the difference in the amount of acid and base added into the dispersion titration (in concentration units) and Δc_{b} is the same for the blank titration. However, since the blank titration generally has little influence on the proton budget at surfaces especially at neutral pH, the term is often ignored (Lützenkirchen et al., 2012a).

3.2. Method 2

The surface proton charge is considered equal to the difference between the amount of acid and base added into solution and the number of protons and hydroxyl groups remaining in the solution (see e.g., Huertas et al., 1998; Rabung et al., 1998; Missana et al., 2003; Rozalén et al., 2009; Liu et al., 2015), which is described by the following equation:

$$\delta_p = [C_a - C_b] - ([H^+]_{\text{meas}} - [OH^-]_{\text{meas}}) \quad (4)$$

where, C_a and C_b are the amounts of acid or base titrant added (mol/L), and $[H^+]_{\text{meas}}$ and $[OH^-]_{\text{meas}}$ are the concentration of protons and hydroxides left in solution (obtained from pH measurements), respectively.

The range of IS values considered here is purposely broad, and as such, the change in the activities of aqueous species must be considered. For the calculation of pH_{PZNPC} through Method 2, because the pH probe measures proton activity, the Debye-Hückel equation (Eqs. (5), (6)) is required to translate the proton activity to the proton concentration (Langmuir, 1997):

$$\log \gamma = -AZ_i^2 \sqrt{I} / (1 + Ba_i \sqrt{I}) \quad (5)$$

$$a = \gamma^* C \quad (6)$$

Both methods were used to model our titration data, as well as estimate the pH_{PZNPC} values for kaolinite, illite and montmorillonite.

To calculate pH_{PZNPC} , the pH value where $\delta_p = 0$ must be identified. In this regard, we selected the positive and negative values that were closest to zero, and then regressed them linearly. The equation of the regression line was subsequently used to extrapolate the pH at which δ_p becomes zero. The extrapolated pH_{PZNPC} values were then averaged based on the triplicate results and standard deviations were calculated to estimate the error.

4. Results

4.1. Titration curves as a function of ionic strength

The titration curves calculated using Method 1 for each of the three clays are shown in Fig. 1. With increasing pH, the surface proton charge of clays decreases due to the progressive deprotonation of surface sites, consistent with previous studies (Avena and Pauli, 1998; Tombácz et al., 2004; Arda et al., 2006; Tertre et al., 2006; Tombácz and Szekeres, 2006; Gu and Evans, 2007, 2008; Gu et al., 2010;). However, our data show no CIP for the titration curves measured at varying solution IS values. As discussed above, previous research has shown that clay minerals have a CIP; however, some of those studies only performed titrations at two ionic strengths (Helmy et al., 1994; Ijagbemi et al., 2009). In our opinion, to better ascertain whether a CIP exists, titrations at more IS values are required. Furthermore, some of the titrations were performed in CO_2 containing systems (Kriaa et al., 2007), in which the influence of aqueous carbonate species on water hydrolysis is taken into consideration for the proton budget of the surface. Although the authors claimed that there is a CIP for kaolinite (Kriaa et al., 2008), the titration curves at varying IS sometimes overlapped with one other, thereby increasing the difficulty in determining the intersection point.

The proton buffering capacity is greater for montmorillonite than illite and kaolinite (in the order of montmorillonite > illite > kaolinite). As shown in Fig. 1, montmorillonite has the highest surface proton charge amongst these three clays while kaolinite has the lowest. For montmorillonite, the titration curves (Fig. 1c) distort at pH 5.0–6.5, while for kaolinite and illite, such behavior does not exist. This may be attributed to the well-known swelling property of montmorillonite, which increases its surface area and thus increases the degree of proton interaction. We also found that this effect is reduced as a function of

increasing IS, which probably indicates that a high electrolyte concentration can inhibit the swelling process or proton adsorption onto the swelled surfaces. Moreover, the titration curves (Fig. 1) for all three clays show a direct relationship with increasing IS, as clays titrated in high IS electrolyte position at the bottom, with lower IS titration curves progressively lying above them. This indicates that at the same pH, the clay in the highest IS solution has the lowest surface proton charge.

4.2. Variation of pH_{PZNPC} with ionic strength

The pH_{PZNPC} values calculated using the two methods are generally the same for kaolinite (Tables 1, 2), increasing from 5.6 to 6.6 as solution IS increases from 0.001 M to 0.1 M. However, more variation is observed between the methods for illite and montmorillonite, with the estimated pH_{PZNPC} values from Method 2 being 0.4 to 0.5 pH units higher than from Method 1. Illite has an average pH_{PZNPC} of between 8.8 and 9.2 using Method 1, but between 9.1 and 9.7 for Method 2, while the pH_{PZNPC} of montmorillonite is calculated to be between 9.6 and 9.8 by Method 1 and between 10.0 and 10.1 using Method 2. Similar to kaolinite, there is a trend of decreasing calculated pH_{PZNPC} with increasing IS. Comparison amongst the three clay minerals shows that the variation amongst the triplicates (standard deviation) for montmorillonite is much larger than that for kaolinite and illite. As mentioned above, the swelling property of montmorillonite likely causes variations in the experimental results.

The variation in calculated pH_{PZNPC} values as a function of ionic strength are illustrated in Fig. 2 for Method 1, and Fig. 3 for Method 2. For all three clay minerals and for both methods, the pH_{PZNPC} values initially decrease sharply with increasing IS at low IS range (0.001 M to 0.025 M). However, with IS increasing (0.025 to 0.1 M), the pH_{PZNPC} changes more slowly. When the pH_{PZNPC} values for all three clays are plotted as a function of $\log(IS)$, a negative linear relationship is observed. The regressed linear relationships for kaolinite (Eq. (7)), illite (Eq. (8)) and montmorillonite (Eq. (9)) are best fit by the following three equations:

$$pH_{PZNPC\text{kaol}} = -0.5084 \log(IS) + 5.142 \quad (7)$$

$$pH_{PZNPC\text{illite}} = -0.1872 \log(IS) + 8.697 \quad (8)$$

$$pH_{PZNPC\text{mont}} = -0.07386 \log(IS) + 9.531 \quad (9)$$

Using Method 2 results in similar linearly decreasing relationships for each clay with $\log(IS)$, which are expressed as:

$$pH_{PZNPC\text{kaol}} = -0.5744 \log(IS) + 4.942 \quad (10)$$

$$pH_{PZNPC\text{illite}} = -0.2956 \log(IS) + 8.968 \quad (11)$$

$$pH_{PZNPC\text{mont}} = -0.06572 \log(IS) + 9.945 \quad (12)$$

The two methods of calculating pH_{PZNPC} produce similar linear relationships between the pH_{PZNPC} and $\log(IS)$, with only small differences in the slope and intercept values of the linear equations for each clay.

5. Discussion

5.1. Differences in the proton interactions between clays and simple oxides

For simple oxides and hydroxides, such as goethite, magnetite, ferrihydrite, gibbsite, and quartz, surface binding sites are amphoteric and can be represented by a generalized surface functional group $\equiv MOH$, where M represents the metal or metalloid that hosts the proton-active hydroxyl moiety. A characteristic feature of titration curves for simple oxides and hydroxides is that at various IS values, the titration curves tend to intersect at one point (CIP), the pH_{PZNPC} (SI Fig. 1), and at that point, the concentration of species $\equiv MOH_2^+$ is, by definition, equal to that of $\equiv MO^-$. At the pH_{PZNPC} , the net surface

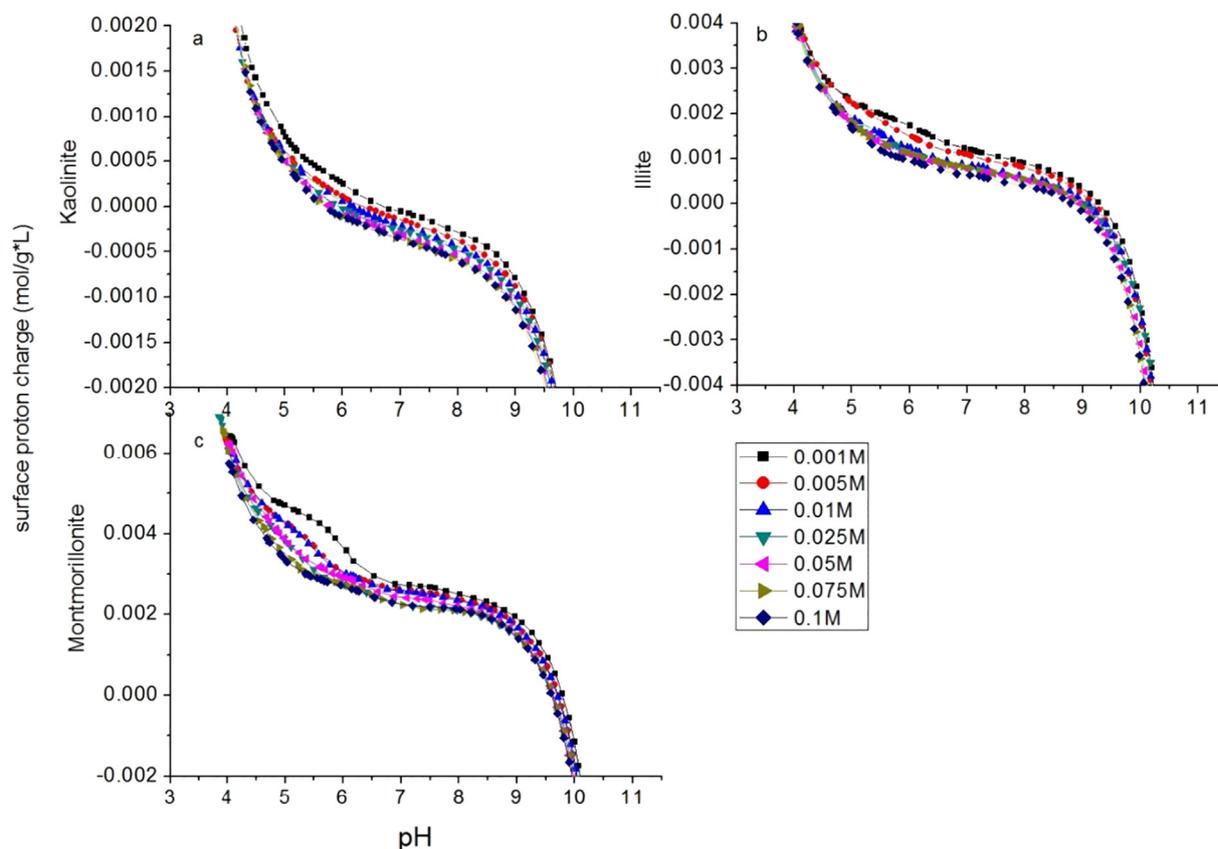


Fig. 1. Potentiometric titration curves for (a) kaolinite, (b) illite, and (c) montmorillonite.

Table 1

PZNPC values calculated using Method 1.

	IS	1 PZNPC	2 PZNPC	3 PZNPC	Ave	Std
Kao Log(IS)						
-3.000	0.001	6.697	6.700	6.623	6.673	0.043
-2.301	0.005	6.128	6.380	6.370	6.293	0.143
-2.000	0.01	6.313	6.148	6.163	6.208	0.091
-1.602	0.025	5.817	6.024	5.934	5.925	0.104
-1.301	0.05	5.747	5.772	5.679	5.733	0.048
-1.125	0.075	5.708	5.772	5.798	5.759	0.046
-1.000	0.1	5.639	5.696	5.687	5.674	0.030
Illite Log(IS)						
-3.000	0.001	9.204	9.290	9.205	9.233	0.050
-2.301	0.005	9.121	9.175	9.148	9.148	0.027
-2.000	0.01	9.084	9.063	9.043	9.063	0.021
-1.602	0.025	9.041	9.049	9.059	9.050	0.009
-1.301	0.05	8.942	8.984	8.944	8.956	0.024
-1.125	0.075	8.834	8.915	8.943	8.897	0.057
-1.000	0.1	8.801	8.830	8.894	8.842	0.048
Mont Log(IS)						
-3.000	0.001	9.790	9.834	9.678	9.767	0.080
-2.301	0.005	9.714	9.591	9.739	9.681	0.079
-2.000	0.01	9.699	9.612	9.718	9.676	0.056
-1.602	0.025	9.674	9.636	9.604	9.638	0.035
-1.301	0.05	9.623	9.536	9.742	9.634	0.103
-1.125	0.075	9.616	9.663	9.603	9.627	0.032
-1.000	0.1	9.597	9.637	9.571	9.601	0.033

Numbers 1, 2, and 3 indicate triplicate titrations; IS means ionic strength; Kao means kaolinite; Mont means montmorillonite; Ave stands for average value of the three sets of PZNPC value; Std stands for the standard deviation of the average value.

Table 2

PZNPC values calculated using Method 2.

	IS	1 PZNPC	2 PZNPC	3 PZNPC	Ave	Std
Kao Log(IS)						
-3.000	0.001	6.684	6.682	6.603	6.657	0.046
-2.301	0.005	6.089	6.345	6.327	6.254	0.143
-2.000	0.01	6.275	6.071	6.118	6.154	0.107
-1.602	0.025	5.711	5.957	5.831	5.833	0.123
-1.301	0.05	5.622	5.658	5.601	5.627	0.029
-1.125	0.075	5.573	5.621	5.655	5.616	0.041
-1.000	0.1	5.500	5.571	5.537	5.536	0.036
Illite Log(IS)						
-3.000	0.001	9.689	9.892	9.792	9.791	0.102
-2.301	0.005	9.513	9.642	9.806	9.653	0.147
-2.000	0.01	9.589	9.607	9.539	9.578	0.035
-1.602	0.025	9.681	9.715	9.518	9.638	0.106
-1.301	0.05	9.246	9.415	9.306	9.322	0.085
-1.125	0.075	9.144	9.246	9.295	9.229	0.077
-1.000	0.1	9.127	9.214	9.279	9.207	0.076
Mont Log(IS)						
-3.000	0.001	10.24	10.25	9.949	10.14	0.170
-2.301	0.005	10.16	10.17	10.01	10.11	0.086
-2.000	0.01	10.16	9.890	10.08	10.04	0.137
-1.602	0.025	10.05	10.21	9.941	10.06	0.135
-1.301	0.05	10.06	9.875	10.12	10.02	0.128
-1.125	0.075	10.09	10.03	10.00	10.04	0.046
-1.000	0.1	10.08	9.968	9.954	10.00	0.066

Numbers 1, 2, and 3 indicate triplicate titrations; IS means ionic strength; Kao means kaolinite; Mont means montmorillonite; Ave stands for average value of the three sets of PZNPC value; Std stands for the standard deviation of the average value.

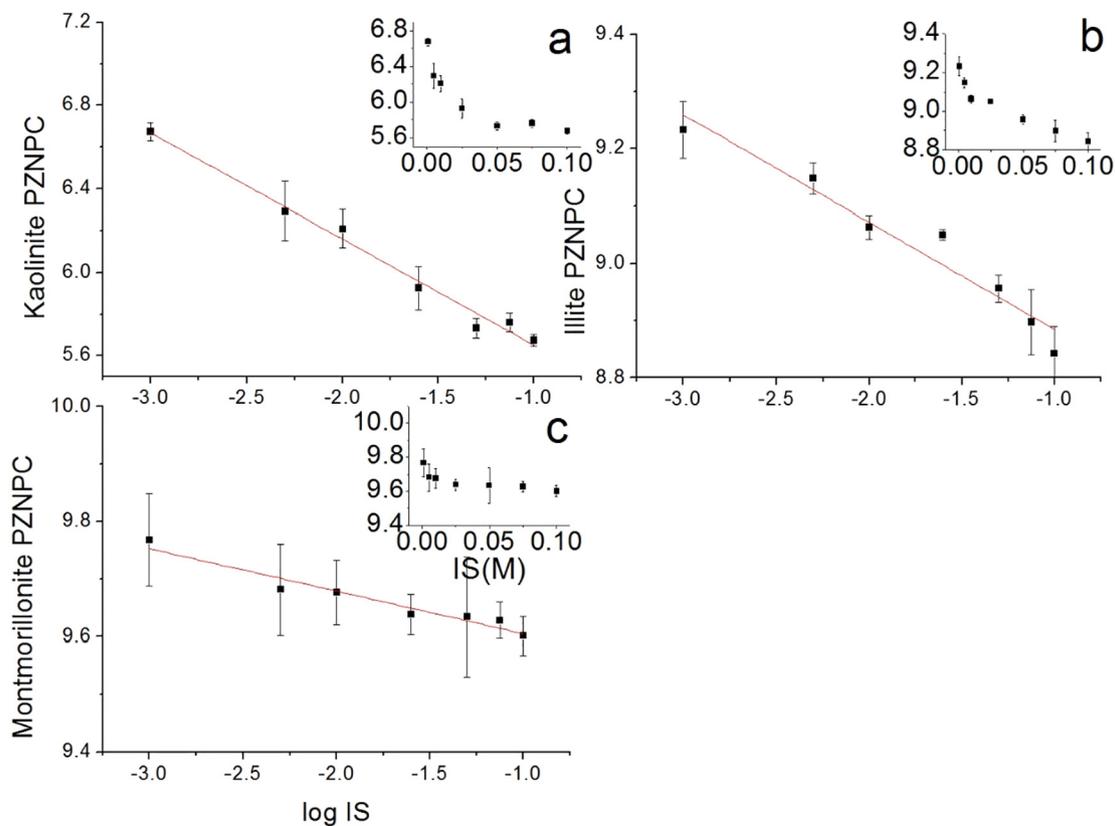


Fig. 2. Changes in the PZNPC using Method 1, as a function of ionic strength (inset plots), and the logarithm of ionic strength, for (a) kaolinite, (b) illite and (c) montmorillonite.

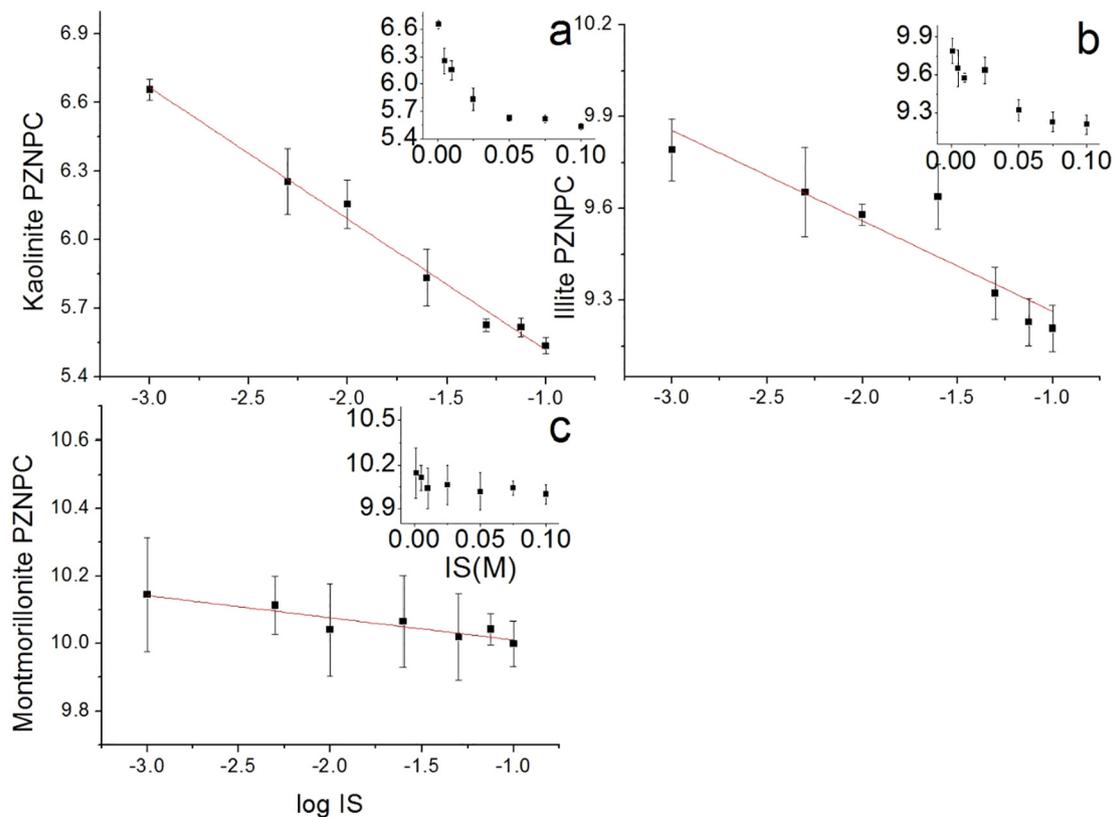


Fig. 3. Changes in the PZNPC using Method 2, as a function of ionic strength (inset plots), and the logarithm of ionic strength, for (a) kaolinite, (b) illite and (c) montmorillonite.

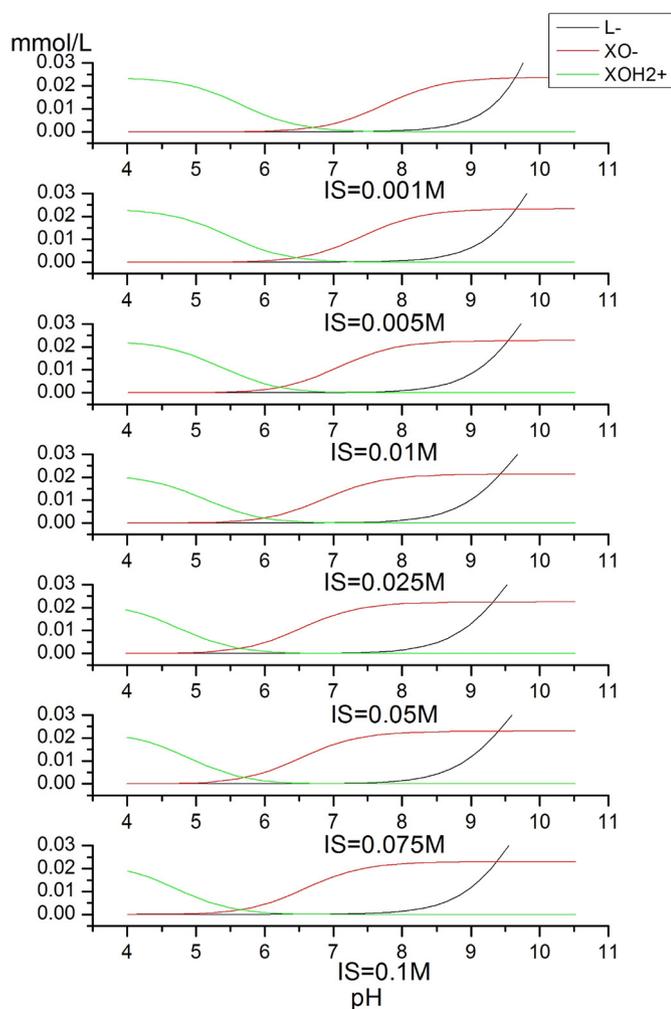


Fig. 4. Speciation diagrams for kaolinite surface sites at the seven IS values tested.

charge is zero, indicating that the surface electric field is zero. Therefore, the solution IS has no impact on the surface electric field. This leads to a common intersection point of titration curves at varying IS (Kraepiel et al., 1998; Lützenkirchen et al., 2012a). Experimental data show this phenomenon: for instance, Peacock and Sherman (2004a, 2004b) performed titrations on goethite at three different IS values (0.1 M, 0.01 M, and 0.003 M), and the curves intersect at pH 8.5 (Peacock and Sherman, 2004a, 2004b), while titration curves for hematite at IS of 0.1 M, 0.01 M, and 0.001 M intersect at approximately pH 6.1 (Rabung et al., 1998). Similar trends have been found for magnetite, ferrihydrite and titanium oxide (Yates and Healy, 1980; Kuo and Hst, 1985; Missana et al., 2003). Collectively, previous studies have demonstrated that at pH values below the pH_{PZNPC} , the surfaces of minerals in higher IS solutions have a higher net proton charge than those in lower IS solutions, while at pH values above the pH_{PZNPC} , the opposite is true (Fig. 4). This pattern can be explained by the impact of IS on the mineral's surface electric field. When $pH < pH_{PZNPC}$, the solid surfaces have a net positive charge, which reduces further adsorption of protons onto the surfaces. However, increasing IS at this pH condition will weaken the positive electrostatic field at the mineral surface and thereby reduce the repulsive force to protons. This effect allows more protons to adsorb onto the surface at high IS conditions as compared to low IS conditions; this likely explains why oxide mineral surfaces have higher surface proton charges at high IS solution conditions when $pH < pH_{PZNPC}$ (SI Fig. 1). Conversely, when $pH > pH_{PZNPC}$, the surfaces of simple oxides are negatively charged favoring proton

adsorption. Thus, the weakening of the net negative electrical field above the pH_{PZNPC} and at high IS causes the mineral surfaces to have less proton charge than they would at lower IS conditions.

Unlike the metal oxides and hydroxides, clay minerals have no CIP as a function of IS. In a pristine system without adsorption of other aqueous ions, clays have two types of surface charge: surface proton charge and permanent structural charge. The surface proton charge of a clay can be described in the same way as above for metal oxides and hydroxides, while permanent charge is mainly due to the isomorphous substitution of higher valent ions by lower valent ions; the latter is a characteristic feature of clay minerals. Generally, trivalent ions (Al^{3+}) in octahedral sheets can be replaced by divalent ions (Mg^{2+}), resulting in one negative charge at the clay surface. This also applies for tetravalent ions (Si^{4+}) in tetrahedral sheets where some are substituted by trivalent ions (Al^{3+}). The permanent charge of clay minerals can only be partially offset by surface protonation/deprotonation reactions, as evident from the observation that the zeta-potentials of kaolinite, montmorillonite and illite increase slightly with decreasing pH, but remain overall negative even at $pH = 2$ (Chorom and Rengasamy, 1995; Vane and Zang, 1997; Kaya and Yukselen, 2005). Therefore, the increase of solution IS for clay systems results in the shielding of the net negatively-charged surface electric field, and thereby lowers proton binding onto the surface across the entire pH range tested (4.0 to 10.5). This explains why the pH_{PZNPC} values for clay minerals decrease systematically with increasing IS (Figs. 2, 3) and why the curves never cross (Fig. 1).

5.2. The pH_{PZNPC} of clay minerals

Both of our methods show that the pH_{PZNPC} of clay minerals changes linearly with logarithm of solution IS, which is in accordance with a previous study by Cao et al. (2016). This relationship may be related to the dynamics of the ion cloud at the mineral surface. According to electric double layer theory, electrolyte ions form a diffuse layer around charged surfaces. This effect will neutralize surface charge and lead to surface potential decrease as a function of distance from surface. The distribution of the surface ion cloud can then be affected by solution ionic strength which results in a decrease of electric double layer thickness with increasing IS (Bohn et al., 2002). Since pH_{PZNPC} is the zero-proton adsorption condition at the surface, its decreasing trend may indicate the thickness of surface electric field varies linearly with the logarithm of IS, with the assumption that the thickness of this double layer is proportional to ion adsorption. Detailed information on this aspect needs further theoretical derivation and experimental evidence.

For the three clays studied here, the pH_{PZNPC} determined for montmorillonite and illite over the seven IS values tested is generally between 9 and 10, while the pH_{PZNPC} for kaolinite is between 5 and 6. Natural water has a pH range between 5 and 8, which is lower than the pH_{PZNPC} of illite and montmorillonite. Thus, under most natural conditions, clay surfaces have a net positive proton charge, i.e., the surfaces are protonated. The structural negative charge of kaolinite is relatively low compared to illite and montmorillonite, which leads to less affinity to protons and a lower pH_{PZNPC} value.

Based on our two methods for calculating pH_{PZNPC} , kaolinite shows the greatest sensitivity to changes in IS (from Figs. 2a and 3a, note that the slope for kaolinite is -0.5 to -0.6), while montmorillonite is the least sensitive (Figs. 2c and 3c shows that the slope for montmorillonite is -0.06 to -0.07). The following reasons may explain the phenomenon above mentioned. Kaolinite's pH_{PZNPC} is at a neutral pH—where there are equal and modest concentrations of H^+ and OH^- ions in solution—making it susceptible to change when modifying the solution proton concentration. This is in contrast to illite and montmorillonite, which have pH_{PZNPC} values at higher pH. Additionally, the tendency for montmorillonite to swell in the presence of water could act as a potential buffer against changes in ionic strength (i.e., $NaNO_3$ and protons

can enter into the interlayers during swelling), and thus impact the change of pH_{PZNPC} with solution IS.

Our pH_{PZNPC} values are slightly higher compared to those in the literature (Kosmulski, 2011) and we believe experimental conditions can account for this discrepancy. The pH_{PZNPC} values of these clays from literature compilation are between 7 and 9 for both illite and montmorillonite (Kosmulski, 2011). The clay pretreatment methods, the source of the clay used and the removal of CO_2 from titration cells may lead to the differences of results. For instance, titration of montmorillonite with an elevated Zn concentration gives pH_{PZNPC} values around 8.8 (Stathi et al., 2009); without pre-bubbling of experimental cell, the pH_{PZNPC} values of montmorillonite are from 8.1 to 7.6 for an IS range between 0.001 M to 0.1 M (Rozalén et al., 2009). It has also been reported that kaolinite pretreated with H_2O_2 at 60 °C with no CO_2 removal procedure has a measured pH_{PZNPC} value of 3.7 (Zhuang and Yu, 2002). Thus, the presence of CO_2 during the titration process is a critical factor in lowering the determined pH_{PZNPC} value. Atmospheric CO_2 can result in a lower pH_{PZNPC} value by forming carbonic acid in water. To prevent this effect, our experimental cell was well sealed to avoid influx of atmospheric CO_2 and bubbled for 30 min with N_2 to ensure that CO_2 initially dissolved into the system was removed, a treatment critical to ensure measurement of a valid pH_{PZNPC} value.

5.3. Surface complexation modeling

Surface complexation modeling (SCM) is a tool that has been used to assess the adsorption capacity of protons and metals onto heterogeneous surfaces in aqueous solution. SCM attributes surface proton charge to proton interactions on discrete surface functional groups, and treats these interactions using balanced chemical reactions. For clay minerals with amphoteric sites ($\equiv\text{MOH}$) and permanently charged sites ($\equiv\text{LH}$), the key protonation and deprotonation reactions can be written as:



It should be noted that the permanently charged sites in clay minerals cannot be satisfied by proton adsorption because they are inherent. Mechanically, they can provide a negative electrostatic field at the mineral surface, which facilitates proton adsorption. However, this “facilitation” effect is hard to represent in a SCM model. Accordingly, we applied a protonated site $\equiv\text{LH}$ to simulate the promotion effect of the surface electrostatic field on proton adsorption. Choosing between an electrostatic model (EM) and a non-electrostatic model (NEM) is also a critical consideration. Electrostatic models distinguish the electrostatic term from bulk adsorption through applying various theories of how surface charge develops (for example, Helmholtz, Gouy-Chapman, Stern theories), in order to derive an intrinsic chemical affinity for the binding of protons or other aqueous species. However, the electrostatic factor is not separated in NEMs, and thus, the result of a NEM is not the intrinsic chemical affinity but can be influenced by changes in the surface electrostatic field. The presence of solution electrolytes may either impact the mineral surface electric field or the affinity of aqueous species for surface functional groups (or both). The purpose of this paper is to investigate the impact of IS on the proton adsorption process; thus, we chose to apply a non-electrostatic model instead in order to explicitly quantify the impact of changes in IS on proton adsorption, and ultimately the pH_{PZNPC} .

Using potentiometric titration data for each of the three clay minerals, the protonation constants and corresponding site concentrations of surface functional groups ($\equiv\text{LH}$, $\equiv\text{XOH}$) can be calculated using the software program FITEQL 4.0 (Westall, 1982). The concentrations of surface species ($\equiv\text{LH}$, $\equiv\text{L}^-$, $\equiv\text{XOH}$, $\equiv\text{XO}^-$, and $\equiv\text{XOH}_2^+$) at each pH point are also listed in the output file and are plotted as a function of pH

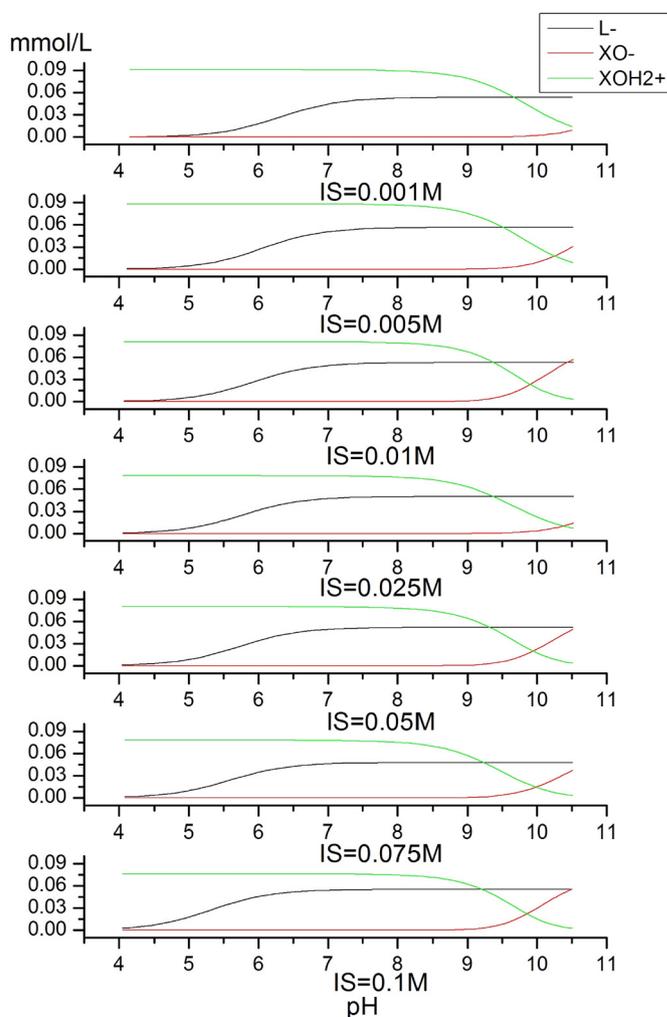


Fig. 5. Speciation diagrams for illite surface sites at the seven IS values tested.

in Figs. 4, 5, 6. Because $\equiv\text{LH}$ and $\equiv\text{XOH}$ groups are uncharged, we can then plot the concentration of $\equiv\text{L}^-$, $\equiv\text{XO}^-$, and $\equiv\text{XOH}_2^+$ with pH and IS to observe how the pH_{PZNPC} value changes with IS.

The $\equiv\text{LH}$ group of kaolinite only begins to deprotonate significantly at $\text{pH} > 8.5$, while for the $\equiv\text{XOH}$ group, the concentration of two species $\equiv\text{XO}^-$ and $\equiv\text{XOH}_2^+$ intersects at approximately pH 6. Since at pH 6 the $\equiv\text{LH}$ group is mainly in a neutral, protonated state (as $\equiv\text{LH}$, with a considerably lower concentration of $\equiv\text{L}^-$ species), the pH at the intersection point of the $\equiv\text{XOH}$ species is nearly equivalent to the value of the pH_{PZNPC} for this clay. We found that the intersection point moves toward lower pH, with increasing IS (Fig. 4), indicating that the pH_{PZNPC} decreases with IS. This is in accordance with the trend uncovered by the two pH_{PZNPC} calculation methods. Illite and montmorillonite behaved differently than kaolinite. For those minerals, the following trends were observed: (1) the species $\equiv\text{L}^-$ and $\equiv\text{XOH}_2^+$ intersect between pH 9 to 10; (2) at the intersection point, the concentration of species $\equiv\text{XO}^-$ is considerably lower than the other two surface species, and thus is not important in determining the overall pH_{PZNPC} ; and (3) the intersection point of species $\equiv\text{L}^-$ and $\equiv\text{XOH}_2^+$, which is nearly equivalent to the pH_{PZNPC} , moves toward lower pH with increasing IS.

Surface species concentrations from the speciation diagrams (Figs. 4–6) were used to calculate pH_{PZNPC} values, using the following equation:

$$\delta_p = [\equiv\text{XOH}_2^+] - [\equiv\text{L}^-] - [\equiv\text{XO}^-] \quad (16)$$

The pH_{PZNPC} of kaolinite calculated with the SCM method is

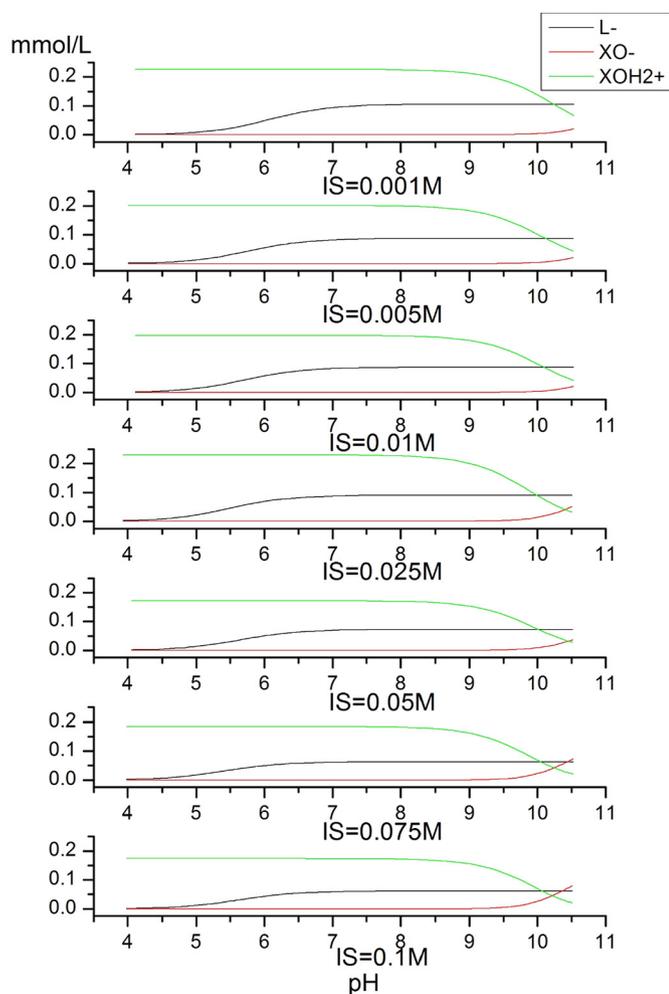


Fig. 6. Speciation diagrams for montmorillonite surface sites at the seven IS values tested.

generally similar to the previous two methods, ranging from 5.6 to 6.7 across the range of IS tested (Table 3). Similar linear trends of the pH_{PZNPC} as a function of the logarithm of IS were observed for each clay using the SCM method (Fig. 7), according to the following relationships:

$$\text{pH}_{\text{PZNPCkaolite}} = -0.5605^* \log(\text{IS}) + 5.073 \quad (17)$$

$$\text{pH}_{\text{PZNPCillite}} = -0.2344^* \log(\text{IS}) + 8.934 \quad (18)$$

$$\text{pH}_{\text{PZNPCmont}} = -0.09864^* \log(\text{IS}) + 9.773 \quad (19)$$

However, the SCM-calculated pH_{PZNPC} values for illite and montmorillonite are between 0.3 and 0.4 pH units higher than those calculated with Method 1, but nearly identical using Method 2. One possible reason for the discrepancy between Method 1 and the latter two methods could be the initial protonation state of the clay minerals. Theoretically, both Method 1 and Method 2 are valid for the calculation of surface proton budget. However, the subtraction between the amount of protons added in a real titration versus the blank titration ignores the fact that the surface could be initially protonated, and that protons pre-existing on the surface can be released into solution. The result is that the calculation of protons adsorbed on surface by Method 1 is likely lower than it is in actuality. This is perhaps the reason why pH_{PZNPC} calculated by Method 1 is lower than the actual conditions. But this cannot be applied to Method 2, because Method 2 calculates the difference between protons added and protons remaining in solution, and in this way the desorption of pre-existing protons is considered in the surface proton budget.

Table 3

PZNPC values calculated using the SCM method.

	IS	1 PZNPC	2 PZNPC	3 PZNPC	Ave	Std
Kao Log(IS)						
-3.000	0.001	nd	6.743	6.699	6.721	0.031
-2.301	0.005	6.111	6.453	6.452	6.339	0.197
-2.000	0.01	6.480	6.229	6.215	6.308	0.149
-1.602	0.025	5.828	6.128	5.987	5.981	0.150
-1.301	0.05	5.709	5.815	5.638	5.721	0.089
-1.125	0.075	5.706	5.780	5.706	5.731	0.042
-1.000	0.1	5.558	5.666	5.642	5.622	0.056
Illite Log(IS)						
-3.000	0.001	9.584	9.725	9.650	9.653	0.070
-2.301	0.005	9.438	9.532	9.477	9.483	0.047
-2.000	0.01	9.316	9.317	9.302	9.311	0.008
-1.602	0.025	9.354	9.363	9.428	9.382	0.040
-1.301	0.05	9.222	9.267	9.263	9.251	0.025
-1.125	0.075	9.134	9.199	9.240	9.191	0.053
-1.000	0.1	9.133	9.184	9.149	9.155	0.026
Mont Log(IS)						
-3.000	0.001	10.19	10.18	9.848	10.07	0.195
-2.301	0.005	10.07	10.10	9.934	10.04	0.089
-2.000	0.01	10.06	9.809	9.958	9.941	0.124
-1.602	0.025	9.915	9.892	9.842	9.883	0.037
-1.301	0.05	9.944	9.768	10.01	9.907	0.125
-1.125	0.075	9.949	9.906	9.852	9.902	0.049
-1.000	0.1	9.928	9.906	9.826	9.886	0.054

Numbers 1, 2, and 3 indicate triplicate titrations; IS means ionic strength; nd means no data, this is because the first titration data did not converge with the SCM method; Kao means kaolinite; Mont means montmorillonite; Ave stands for average value of the three sets of PZNPC value; Std stands for the standard deviation of the average value.

6. Conclusions and environmental implications

Our work demonstrates that acid-base titration curves for kaolinite, montmorillonite and illite at different IS have no CIPs. This indicates that the change of clay surface reactivity and pH_{PZNPC} is a function of solution IS. By then using three different methods to calculate the pH_{PZNPC} of three clay minerals, we additionally observed that pH_{PZNPC} decreases linearly with increasing solution IS. The pH_{PZNPC} values calculated by the SCM method are around 0.3 to 0.4 pH units higher than those calculated with Method 1 but are generally in accordance with Method 2 for montmorillonite and illite. For kaolinite, SCM-calculated pH_{PZNPC} values are approximately the same as those calculated using the above two methods.

The study of changes in the pH_{PZNPC} of clay minerals with ionic strength has important environmental implications. Clay particles originally released to streams characterized by low IS and slightly acidic waters may eventually be discharged into estuaries with more alkaline pH and higher IS. One of the goals of our future research is to then ascertain whether clay minerals deposited in estuaries serve as trace metal sinks or sources to the overlying water column. Although this work is currently being conducted, there are existing data available that consider clay mineral reactivity in such settings. For instance, experimental results of Cd adsorption onto montmorillonite showed that almost 90% of Cd adsorbed onto montmorillonite at pH = 6 and at 0.001 M ionic strength (Gu et al., 2010), while this number decreased to only 10% if ionic strength was increased to mimic seawater (0.56 M) (Liu et al., 2018). The increase of pH has inverse effect with IS, where the increase of pH from 6 to 8 results in an additional 40% of Cd adsorption (Liu et al., 2018). The overall budget of Cd in estuary environment could be more complicated when considering activity of Cd and its aqueous complexation with carbonate and hydroxide groups. Future work could specific this problem, but the empirical relationships we have developed here can be used in consort with surface complexation models to quantitatively account for changing proton binding

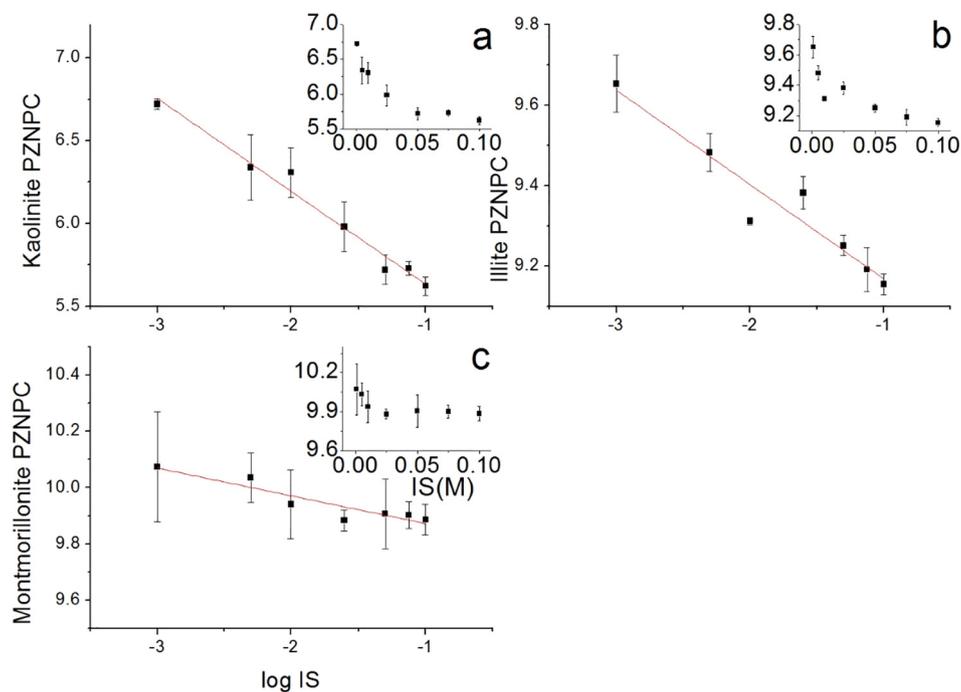


Fig. 7. Changes in the PZNPC using the SCM method as a function of ionic strength (inset plots), and the logarithm of ionic strength, for (a) kaolinite, (b) illite and (c) montmorillonite.

behavior as pH and solution IS conditions change.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemgeo.2018.06.023>.

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