Sensitivity of the acid–base properties of clays to the methods of preparation and measurement

1. Literature review

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Abstract

Measuring and modeling the surface charge of clays, and more especially smectites, has become an important issue in the use of bentonites as a waste confinement material aimed at retarding migration of water and solutes. Therefore, many studies of the acid–base properties of montmorillonite have appeared recently in the literature, following older studies principally devoted to cation exchange. It is striking that beyond the consensus about the complex nature of the surface charge of clays, there are many discrepancies, especially concerning the dissociable charge, that prevents intercomparison among the published data. However, a general trend is observed regarding the absence of common intersection point on raw titration curves at different ionic strengths. Analysis of the literature shows that these discrepancies originate from the experimental procedures for the preparation of the clays and for the quantification of their surface charge. The present work is an attempt to understand how these procedures can impact the final results. Three critical operations can be identified as having significant effects on the surface properties of the studied clays. The first one is the preparation of purified clay from the raw material: the use of acid or chelation treatments, and the repeated washings in deionized water result in partial dissolution of the clays. Then storage of the purified clay in dry or wet conditions strongly influences the equilibria in the subsequent experiments respectively by precipitation or enhanced dissolution. The third critical operation is the quantification of the surface charge by potentiometric titration, which requires the use of strong acids and bases. As a consequence, besides dissociation of surface sites, many secondary titrant consuming reactions were described in the literature, such as cation exchange, dissolution, hydrolysis, or precipitation. The cumulated effects make it difficult to derive proper dissociation constants, and to build adequate models. The inadequation of the classical surface complexation models to describe the acid–base behavior of clays is illustrated by the electrokinetic behavior of smectites, which is independent from the pH and the ionic strength. Therefore, there is still a need on one hand for accurate data recorded in controlled conditions, and on the other hand for new models taking into account the complex nature of the charge of clays.

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Keywords: Clay; Montmorillonite; Potentiometric titration; Surface charge; Electrokinetics

1. Introduction

The electric surface charges of clays govern characteristic chemical and physical phenomena such as ion exchange, adsorption, swelling, colloidal stability, and flow behavior. These phenomena are of primary importance in environmental chemistry, since clays are ubiquitous minerals, and are involved in plant nutrition, stability of agricultural soils, and transport of pollutants. In the mineral industry, many processes require controlled behavior of clay dispersions, e.g., the injection of slurries in the ceramics industry or the versatile flow properties of drilling muds. The use of ben-
tonites as a confinement material in waste repositories is of great interest because of the swelling, low permeability, and migration-retarding properties of the constituting montmorillonite. To that purpose, an extensive and accurate knowledge of the surface properties of montmorillonites is basically required in order to obtain the parameters for long-term prediction of the barrier performances. This is particularly important for the confinement of nuclear wastes, where the critical time domain covers thousands of years. It is thus not surprising that during the past decades, a number of works were devoted to measuring and modeling the surface charge of clays. The most studied clay is montmorillonite, the constituting mineral of bentonite.

The origin of the electrical charge of montmorillonite is of two kinds: on one hand substitutions in the crystalline network, and on the other hand broken-bond atoms at the edge surfaces [1]. Charge-imbalanced substitutions in the crystalline network, e.g., Al$^{3+}$ for Si$^{4+}$ in tetrahedral coordination, or Mg$^{2+}$ for Al$^{3+}$ in octahedral coordination, result in positive charge defects, i.e., net negative charges, the amount of which is directly related to the amount of substitutions. The location and amount of substitutions is the key to the mineralogical classification of the 2:1 phyllosilicates (Table 1). The structural charges of clays are called permanent charges because they are independent of the physicochemical conditions in the surrounding medium. Although the structural charges are not in direct contact with the solution, they give rise to a negative electric potential, which is compensated for by an electrostatically attracted interlayer of exchangeable cations.

Edges are the faces of the phyllosilicate particle where crystal growth occurs. Vacant coordinations on the outermost oxygens and hydroxyls bind to the metal cations (Si, Al, Mg) give rise to an electric charge on which dissociation–complexation reactions occur. The value of this local charge is most often considered as an integer value (−1, 0, or +1) in the framework of the classical 2-pK surface-charging model [2–7]. In the more recent 1-pK model, based on Pauling’s concept of formal charge [8–10], the local charge is defined as fractional, according to the mono-, di-, or tri-coordinated character of the outermost oxo- or hydroxo-groups. This principle is the basis of the multisite complexation (MUSIC) model developed by Hiemstra and co-workers [11–13]. Due to the lamellar morphology of montmorillonite particles, the quantitative distribution of structural and dissociable charges is about 90–95% and 5–10%, respectively [14]. The quantitative predominance of the structural charges in montmorillonite may explain that in the past four decades, a vast majority of studies related to ion adsorption were devoted to the mechanisms of cation exchange. However, the proton adsorption on clays is gaining in interest, and a growing number of studies were recently devoted to this topic, often as a prerequisite to the understanding of the adsorption of metals or lanthanides [15–26].

Experimental determination of the dissociable charge of clays is usually based on potentiometric titration which yields the pristine proton charge (Table 2), and electrokinetic measurements which give access to the electric potential of the diffuse layer of counterions. These methods are indirect, and yield global data on the studied systems. Molecular-scale measurement of the local surface reactions is still difficult to perform. Although recent attempts succeeded in quantifying the dissolution processes in situ using atomic force microscopy [27] and investigating the particle–particle interactions [28,29], local measurements of charging phenomena are still lacking.

Accurate acid–base constants of clays are difficult to obtain experimentally, because of other side-reactions in-

### Table 1

Classification of phyllosilicates according to the localization and abundance of crystalline lattice substitutions

<table>
<thead>
<tr>
<th>Charge ($x$) moles per half unit cell</th>
<th>1:1 Sheet</th>
<th>2:1 Sheet</th>
<th>Smectites</th>
<th>Micas</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kaolinite</td>
<td>Al$_2$Si$_2$(O$_5$)(OH)$_4$</td>
<td>Pyrophyllite</td>
<td>Al$_2$Si$<em>4$(O$</em>{10}$)(OH)$_2$</td>
</tr>
<tr>
<td></td>
<td>Serpentine</td>
<td>Mg$_3$Si$<em>2$(O$</em>{10}$)(OH)$_4$</td>
<td>Hectorite</td>
<td>Mg$_3$(Si$_4$–$x$Al$<em>x$)(O$</em>{10}$)(OH)$_2$(CEC)$_x$</td>
</tr>
<tr>
<td></td>
<td>Talc</td>
<td>Mg$_3$(Si$_4$–$x$Al$<em>x$)(O$</em>{10}$)(OH)$_2$(CEC)$_x$</td>
<td>Saponite</td>
<td>Mg$_3$(Si$_4$–$x$Al$<em>x$)(O$</em>{10}$)(OH)$_2$(CEC)$_x$</td>
</tr>
<tr>
<td></td>
<td>Montmorillonite</td>
<td>(Al$_2$–$x$Mg$_x$)Si$<em>4$(O$</em>{10}$)(OH)$_2$(CEC)$_x$</td>
<td>Beidellite</td>
<td>Al$<em>2$(Si$</em>{4–x}$Al$<em>x$)(O$</em>{10}$)(OH)$_2$(CEC)$_x$</td>
</tr>
<tr>
<td></td>
<td>Hectorite</td>
<td>(Mg$_3$–Li$_x$)Si$<em>4$(O$</em>{10}$)(OH)$_2$(CEC)$_x$</td>
<td>Tetraedral substitutions</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Montmorillonite</td>
<td>(Al$_2$–$x$Mg$_x$)Si$<em>4$(O$</em>{10}$)(OH)$_2$(CEC)$_x$</td>
<td>Illite</td>
<td>(Al$<em>{1.75}$R$<em>x$)Si$</em>{3.5}$Al$</em>{0.5}$(O$_{10}$)(OH)$<em>2$K$</em>{0.75}$</td>
</tr>
<tr>
<td></td>
<td>Hectorite</td>
<td>(Mg$_3$–Li$_x$)Si$<em>4$(O$</em>{10}$)(OH)$_2$(CEC)$_x$</td>
<td>Vermiculite</td>
<td>(MgFe$<em>3$)(Si$</em>{4–x}$Al$<em>x$)(O$</em>{10}$)(OH)$_2$Mg$_x$</td>
</tr>
<tr>
<td></td>
<td>Montmorillonite</td>
<td>(Al$_2$–$x$Mg$_x$)Si$<em>4$(O$</em>{10}$)(OH)$_2$(CEC)$_x$</td>
<td>Glauconite</td>
<td>(Al$<em>{1.75}$Fe$</em>{3–x}$Al$<em>x$)(O$</em>{10}$)(OH)$_2$K</td>
</tr>
<tr>
<td></td>
<td>Hectorite</td>
<td>(Mg$_3$–Li$_x$)Si$<em>4$(O$</em>{10}$)(OH)$_2$(CEC)$_x$</td>
<td>Chlorite</td>
<td>(MgFe$<em>3$)(Si$</em>{4–x}$Al$<em>x$)(O$</em>{10}$)(OH)$_2$K</td>
</tr>
<tr>
<td></td>
<td>Montmorillonite</td>
<td>(Al$_2$–$x$Mg$_x$)Si$<em>4$(O$</em>{10}$)(OH)$_2$(CEC)$_x$</td>
<td>Muscovite</td>
<td>Al$<em>2$(Si$</em>{3}$Al)(O$_{10}$)(OH)$_2$K</td>
</tr>
<tr>
<td></td>
<td>Hectorite</td>
<td>(Mg$_3$–Li$_x$)Si$<em>4$(O$</em>{10}$)(OH)$_2$(CEC)$_x$</td>
<td>Biotite</td>
<td>(Mg,Fe$<em>{3–x}$)(Si$</em>{3}$Al)(O$_{10}$)(OH)$_2$(K)</td>
</tr>
</tbody>
</table>

**Notes:**
- 1:1 Sheet represents dioctahedral phyllosilicates.
- 2:1 Sheet represents trioctahedral phyllosilicates.
- Smectites include Montmorillonite, Hectorite, Beidellite, Saponite, Glauconite, Phlogopite, Vermiculite, Illite, Glauconite, Muscovite, and Biotite.
- Micas include Kaolinite, Pyrophyllite, and Talc.
- The charge ($x$) represents the number of substitutions per half unit cell.
volving $\text{H}^+$ and $\text{OH}^-$, ions besides dissociation and ion complexation: ion exchange, dissolution, precipitation, and readsoption. These processes are cumulative and are even more complicated in the presence of secondary minerals if the bentonite is studied as a whole. Therefore, extraction and purification procedures are most often applied, with the risk that these procedures may alter the clay surface and bias the titration curves [30]. The great differences in the titration curves, and subsequently in the calculated thermodynamic constants that are observed in the literature most often come from differences in the protocols used by the authors.

As far as modeling is concerned, there is still no consensus about the factors to be taken into account. In particular, the absence of a common intersection point on the titration curves at various ionic strengths prevents direct application of the classical double layer and surface complexation models, and requires taking into account the structural charge [25,31,32]. Unfortunately, there is still a lack of complete and reliable experimental data sets by which the models could be constrained, as already pointed out by Avena and De Pauli [31]. Typical shortcomings are, for example, improperly prepared material, titration curves recorded for only one ionic strength, or titration conditions involving extreme pH.

The aim of the present paper is to analyze the impact of the experimental procedures on the titration curves and dissociation constants of montmorillonite and other 2:1 clays published in the literature. Three critical aspects are examined: the preparation and storage of the clay, the experimental conditions for the quantification of the surface charge from potentiometric study, and the electrokinetic behavior of clay particles. The companion paper [33] is devoted to the experimental quantification of these effects.

### 2. Effects of clay preparation

Occurrence of pure and homogeneous clays is extremely rare in nature. Clays are formed by the degradation of parent rocks by geochemical and/or hydrothermal evolution, or by weathering in the presence of humic substances during the formation of soils [1]. In the first case, clay-rich deposits sometimes of huge extent (e.g., Wyoming bentonite) are encountered. In soils, clays minerals are mixed with other minerals and organic matter. In all cases, the study of the clay mineral requires previous purification.

Depending on the initial material, two types of purification procedure are used. Sedimentary deposits are generally rich in clay minerals (up to 90%), and the purification requires chiefly dispersion in water and decarbonation, either with a strong acid such as $\text{HCl}$ at pH 3–3.5 or with a weak acid such as acetate at pH 4–5. Obtaining soil clays requires dispersion, decarbonation, and extraction of the clay-rich size fraction ($<$2 µm) by sedimentation. Peroxide treatment is sometimes carried out to eliminate the organic matter. Several authors also use specific treatments to eliminate iron and aluminum (oxyhydr)oxide phases. Chelating agents such as the oxalate buffer [34,35] are used to remove the crystalline phases selectively. The reducing and chelating buffer citrate–dithionite–bicarbonate [36] is used to remove the iron oxides selectively. However, such procedures using chelating agents may alter the clay by partial or noncongruent dissolution. This is why Baeyens and Bradbury [16] rejected application of these methods to the purpose of investigating acid–base properties of clays.

In most cases, homoionization of the clay is achieved by exchange with the appropriate salt solution. Finally, the salinity and the acidic or basic impurities of the suspension are eliminated by washings or by dialysis against demineralized water. A comparative study of the titration curves carried out at two stages of the purification process [37] shows the crucial effect of washing on the relative position of charge curves (Fig. 1). After acid treatment, the PZNPC (see Section 3.3 for the definition) ranged between 4 and 5, and after subsequent washing they were shifted toward pH 8. The complete purification procedure is mostly used by authors who intend to study the properties of the clay mineral, whereas other authors investigate the raw material or homoionized material [38–40].

Purified material is most often stored after drying in an oven between 60 and 80°C [37,41] or after freeze-drying [22]. On the other hand, some authors prefer to store the concentrated suspension at low temperature to avoid microbial activity and under argon in the appropriate salt solution to prevent carbonation and ion exchange [14,16,31,32,42,43]. Verburg and Baveye [44] mention a possible effect of drying on the hysteresis of cation exchange curves on montmorillonite, but there was as yet no study specifically devoted to the effect of drying of the clay sample on the titration curves.

### Table 2

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Name</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZNPC</td>
<td>Point of zero net proton charge</td>
<td>Intersection between raw titration curve for the blank and for the suspension</td>
</tr>
<tr>
<td>PZSE</td>
<td>Point of zero salt effect</td>
<td>Intersection between charge curves at different electrolyte concentrations</td>
</tr>
<tr>
<td>PZC</td>
<td>Point of zero charge</td>
<td>Common intersection point where both PZNPC and PZSE coincide</td>
</tr>
<tr>
<td>IEP</td>
<td>Isoelectric point</td>
<td>pH of zero $\zeta$ potential on electrokinetic curves</td>
</tr>
</tbody>
</table>
3. Quantification of the surface charge of clays from potentiometric titration

3.1. Experimental procedures

The proton charge of clays (Table 2) is experimentally determined by acid–base potentiometric titration, after the methodology developed in early works by Bolt [45] and Parks and De Bruyn [46] for metal oxides. The amount of surface hydroxyls protonated or deprotonated as function of the pH and the ionic strength of the electrolyte is calculated for each titration point by difference between the volume of titrant (acid or base solution) added to the suspension and a reference volume. The reference data used by the different authors are of three kinds: the concentration of H\(^+\) and OH\(^-\) ions deduced from the equilibrium pH, the titration of the particle free electrolyte solution, or the titration of the electrolyte solution previously equilibratated with the clay.

Different titration procedures are reported in the literature: continuous titration or batch titration. Continuous (or stepwise, or rapid) titration consists in adding small amounts of titrant successively to a suspension of the solid under study. This method is generally automated, and yields titration curves with numerous data points. However, the equilibrium condition required before adding the next increment is crucial. Short delays may result in nonequilibrium, whereas long delays favor the dissolution of the solid and increase the experimental error due to the drift of the pH electrode. An inherent advantage of this continuous method is the possibility of recording potentiometric titration curves at different ionic strengths on the same suspension after addition of an adequate electrolyte amount between two titrations, as done for glauconite [47].

Conversely, batch titration consists in preparing different suspensions at various initial pH and in measuring the pH at equilibrium, most often after 24 h [16]. Batch titration is usually affected by increased cumulative experimental error compared to continuous titration (solid amount, volumes, carbonatation of the solutions). A great advantage of batch titration is that different analytical methods can be used to quantify side processes involving proton/hydroxide consumption that could occur during the equilibrium. For example, the dissolution processes were estimated from the resulting speciation of elements in solution [16,48]. This calculation is based either on the resulting amounts of elements and their thermodynamic acid–base data, or from back titration. The latter approach [38,48] consists in titrating the equilibrated supernatants back to the initial pH, in order to take into account the titrant consumption by the side reactions, quantified by difference between the initial amount of added titrant and the amount used for back titration. Anyway, it is important to point out that most authors did not consider the possible sorption or precipitation of soluble species which at the end will not appear in the final balance of soluble species.

3.2. Side reactions during titration of clay particles

Despite the apparent simplicity of the potentiometric titration method, many parameters must be controlled in order to extract information relevant to the surface charge of solids. As far as clays are concerned, several secondary processes significantly contribute to the consumption of H\(^+\) and OH\(^-\) ions: cation exchange at acidic pH between the protons and the exchangeable cations, dissolution of the clay at acidic or alkaline pH, readsorption of dissolved species though complexation or cation exchange, speciation, and hydrolysis of dissolved species.

3.2.1. Cation exchange

The contribution of cation exchange on the proton consumption can be evaluated using the selectivity coefficient \(K_s\). For an exchange reaction of the type \(\text{XCt} + \text{H}^+ \leftrightarrow \text{XH} + \text{Ct}^+\), the selectivity coefficient is \(K_s = ([\text{Ct}^+]/[\text{XH}]/[\text{H}^+]/[\text{XCt}]\), where \(\) indicate concentrations and \(\) surface densities. The selectivity coefficient of the proton versus Na\(^+\) is 1.26 [49]. In an electrolyte solution at 1, 10, and 100 mmol L\(^-1\), the consumption of H\(^+\) consecutive to H\(^+\)–Na\(^+\) exchange contributes then about 5% of the CEC for pH 4, 3, and 2, respectively. For montmorillonite, where it is generally admitted that the proton charge represents approximately 5% of the total charge [14,50], which implies that under the latter conditions, the amount of exchanged protons is equivalent to the amount adsorbed on the protonated sites. Therefore, cation exchange can be neglected only when using high electrolyte concentrations (> 10 mmol L\(^-1\)) and moderately acidic conditions (pH > 4) [16]. One drawback of doing so is to cause coagulation of the clay suspension, since the critical coagulation concentration of montmorillonite is typically close to 20 mmol L\(^-1\) [51]. Aggregation of the clay may reduce the accessibility of the surface sites, or at least retard the diffusion kinetics.
Measurement of the CEC as a function of the pH was recently suggested to be an effective method to indirectly determine the acid–base properties of clays. Tournassat et al. [48] showed linear relationships between the variation of proton consumption and the CEC of montmorillonite in the pH range 4–11. Such behavior was associated with concomitant proton dissociation of edge surface sites and equivalent sodium sorption as counterions. Note that such experiments were mostly carried out under air and in batch conditions.

3.2.2. Dissolution and related effects

Interpretation of the potentiometric data is complicated by the dissolution of the solid phase, which strongly affects the H⁺/OH⁻ balance. The dissolution of smectites is not well understood, and the solid phases that control the activity of dissolved species have not been unambiguously identified [52]. One of the most relevant studies of montmorillonite dissolution according to the pH at room temperature was carried out by Baeyens and Bradbury [16]. These authors showed that the amounts of dissolved Al, Si, and Fe were systematically below the solubility of the corresponding pure minerals, quartz, gibbsite, and amorphous ferric oxide (Fig. 2). Surprisingly, the concentration of dissolved Mg was not measured in this study.

Correction of the effect of dissolution is most often achieved by subtracting the titration curve of the equilibrated supernatant from the titration curve of the suspension [50]. The reference titration curve can also be modeled using the speciation constants of the dissolved species [39]. However, this method does not take into account the variation of the amount of dissolved species according to the pH. Also the presence of colloidal species in the reference solution may strongly interfere with such measurements. Another method consists in calculating the reference curve directly from the solubility constants of the pure minerals [14]. Titration curves corrected for the solubility of the mineral were also carried out by Huertas et al. [53] on kaolinite, and by Lefevre et al. [54] and Tombacz and Szekeres [55] on γ- and δ-aluminas, respectively. The studies by Baeyens and Bradbury [16] and Tournassat et al. [48] show that for montmorillonite the dissolved amounts are very low for pH ranging between 4 and 10, of the order of magnitude more than the predicted soluble Al³⁺ in equilibrium with gibbsite. Dissolution of such amounts mobilizes up to 30% of the consumed H⁺ at pH 4.

Fig. 2. Concentrations of Si, Al, and Fe in the supernatant of SWY1 montmorillonite in NaClO₄ 0.5 M after (○) 1 day, and (●) 7 days contact. The dotted lines represent the calculated solubilities of quartz, amorphous iron oxide, and gibbsite, respectively. Data from Baeyens and Bradbury [16].

The chemical evolution of dissolved ionic species affects the H⁺/OH⁻ balance since a part of the added titrant is consumed by hydrolysis reactions (Table 3). Quantification of this contribution from the pH and the amounts of released elements is theoretically possible by using the corresponding thermodynamic constants. Such an approach was followed by Liu [39] and Lu and Smith [40] by introducing the interactions between soluble Al³⁺ and H₂SiO₄ in the model calculations. However, in the general case, the above aspects are only rarely taken into account in the acid–base studies on clays, despite the variety aqueous monomeric, polymeric, and combined species that may be formed during titration.
Some equilibrium constants (− \log K) of the speciation in solution of potentially elements released in solution by clay dissolution

<table>
<thead>
<tr>
<th>Solution reactions</th>
<th>−\log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂SiO₄ = H₂SiO₄⁻ + H⁺</td>
<td>9.9</td>
</tr>
<tr>
<td>H₂SiO₄ = H₂SiO₄⁻ + 2H⁺</td>
<td>22.5</td>
</tr>
<tr>
<td>Al³⁺ + H₂O = AlOH₂⁺ + H⁺</td>
<td>5.0</td>
</tr>
<tr>
<td>Al³⁺ + 2H₂O = Al(OH)₄⁻ + 2H⁺</td>
<td>9.3</td>
</tr>
<tr>
<td>Al³⁺ + 3H₂O = Al(OH)₃ + 3H⁺</td>
<td>14.9</td>
</tr>
<tr>
<td>Al³⁺ + 4H₂O = Al(OH)₃ + 4H⁺</td>
<td>22.9</td>
</tr>
<tr>
<td>Fe²⁺ + H₂O = FeOH⁺ + H⁺</td>
<td>9.5</td>
</tr>
<tr>
<td>Fe²⁺ + 2H₂O = Fe(OH)₂ + 2H⁺</td>
<td>20.5</td>
</tr>
<tr>
<td>Fe²⁺ + 3H₂O = Fe(OH)₃ + 3H⁺</td>
<td>31.9</td>
</tr>
<tr>
<td>Fe²⁺ + 4H₂O = Fe(OH)₄ + 4H⁺</td>
<td>46.3</td>
</tr>
<tr>
<td>Mg²⁺ + H₂O = MgOH⁺ + H⁺</td>
<td>11.4</td>
</tr>
</tbody>
</table>

* Data from Stumm and Morgan [68].

3.3. Charging behavior and characteristic points (PZNPC, PZC, PZSE)

On simple oxides and in the presence of an indifferent (1:1) electrolyte, the curves corresponding to different ionic strengths should display characteristic intersection points that define the acid–base properties of the solid. The definitions given by Sposito [56,57] are used in the present work (Table 2).

A vast majority of studies of 2:1 clays report the absence of a common intersection point such as a PZSE (Fig. 3), in conflict with the commonly observed behavior of simple oxides. Instead, the titration curves are quite parallel, and the PZNPC decreases in pH according to increasing ionic strengths. The shift of the titration curves observed for montmorillonites and illites is usually attributed to some effect of the permanent structural charge. Avena and De Pauli [31] found for montmorillonite a linear relationship between the position of the PZNPC and the logarithm of the ionic strength. More recently Avena et al. [32], following earlier work by Beene et al. [37] on illites, showed that the structural charge of 2:1 clays can exert a direct influence on the dissociation of the edge sites, since the statistical distance of the substituted octahedra from the edges (7–9 Å for montmorillonites) is close to the distance from the faces (about 5 Å) and smaller than the Debye length (30 Å for I = 0.01 molL⁻¹). It can then be postulated that the amplitude of the PZNPC shift depends on the rate of structural substitutions. This is verified in Fig. 4, where PZNPCs of montmorillonites and illites collected in the literature are plotted versus the logarithm of the ionic strength. The linear relationship described by Avena and De Pauli [31] is confirmed, and the slopes of the straight lines are significantly higher for illites (average −0.73) with about 1.4 substitutions per unit cell than for montmorillonites (average −0.49), with about 0.8 substitutions per unit cell.

Recently, models were proposed in order to take into account the effect of the lattice charge on the proton charge of clays. Using a model that combines protonation–deprotonation reactions, cation exchange and electrical double layer, Avena and De Pauli [31] show that a fraction of the structural charge is not screened by cations and that this fraction is responsible for the negative zeta potential (see next section) and modifies the normal behavior of variable

![Fig. 3. Influence of ionic strength on titration curves of montmorillonites. (i) NaCl, (■) 0.006 M, (○) 0.014 M, (▲) 0.088 M. Data from Avena and De Pauli [31]. (ii) NaClO₄, (△) 0.1 M after 1 day, (●) 0.5 M after 1 day, and (□) after 7 days. Data from Baeyens and Bradbury [16].](image-url)
charge so that the PZNPC shifts by changing the electrolyte concentration. From their model of the clay–water interface, Kraepiel et al. [25] show that when the edge charge is slightly positive, a decrease in ionic strength causes the potential generated by the structural charge to become more negative, and dominant over the decreased shielding in solution. However, there is yet no consensus about the mechanism by which the structural charge influences the PZSE of montmorillonite and illite.

In the absence of a PZSE for montmorillonite, several studies considered the PZNPC of a unique titration curve as the PZC. As a consequence, the values of PZC that can be found in literature for montmorillonite range from pH 5.5 to 8.5. This broad scatter is reflected in the values of the thermodynamic constants derived from dissociation and surface complexation models, which prevents from drawing a precise picture of the surface dissociation constants of clays. The published pK values are spread over 10 pH units. However, a purely statistical analysis of these data without any consideration of the model or parameters used, reveals a specific trend in the distribution of the pKs (Fig. 5). The most frequently found pK values are located in three domains: pH 4–5, pH 6–8, and pH 10–11. Acidic pKs are generally attributed to the tetrahedral sites, and alkaline pKs to the octahedral sites. Such assignment relies most often on the simplistic analogy with the points of zero charge of silica (pH 2–4) and gibbsite (pH 8–10).

4. Electrokinetics of clay particles

Additional information on the surface charge of clays is obtained from electrokinetic measurements, most often electrophoresis. Electrokinetic methods yield the potential of the diffuse layer, the ζ potential. According to the Stern model of the double layer, the ζ potential corresponds to the part of the surface potential which is not neutralized by the counterions adsorbed in the Stern plane. Among the numerous electrokinetic measurements on montmorillonites and other 2:1 clays, there is a general agreement that their ζ potential is negative (−30 to −50 mV) within a broad pH domain from 2 to 12, independently of the ionic strength, and that no isoelectric point (the pH of zero ζ potential: IEP) is observed [31,60–64]. These observations clearly indicate that the electrokinetic potential is dominated by the permanent layer charge, which is by nature independent from the external conditions. For montmorillonite, the contribution of the acid–base charges to the overall surface charge is a priori negligible, since the edges represent 5–10% of the total surface area because of the strong anisotropy of the particles. However, in a systematic electrokinetic study of 2:1 clays, Thomas et al. [65] showed that the edge charges are dominant in nonexpandable clays such as talc or smectites with their charge artificially reduced by thermal migration of interlayer cations (Hofmann–Klemen effect), and in highly substituted clays such as illites. In these clays the face–face interactions are strongly attractive, and result in large stacks of clay platelets. The electrokinetic potential of such clays is then dominated by the dissociation of the edge sites, and is expected to vary with the pH. This is observed in Fig. 6 an isoelectric point is observed at pH 2–3. At opposite, the medium-charged samples of montmorillonite (0.65) and saponite (0.7 and 1.2) display stable ζ potential over the studied pH range.
The very particular electrokinetic behavior of clays, and especially smectites, is still a matter of debate on several points. First, the structure of the clay–electrolyte interface, as described by the electrical double-layer theory, is still unclear. Since the surface charge is mainly due to structural substitutions, and not to dissociated sites, the counterions are only attracted by electrostatic forces, and the Stern layer should not form. The electrokinetic potential would then be much stronger than the −50 mV generally observed, and should be related to the amount and localization of layer charge, which is not observed [63,65]. On the opposite, if one considers that the amount of counterions exactly balances the surface charge, as usually observed by chemical analysis, a strongly developed Stern layer must be admitted. In turn, this would imply zero electrokinetic potential. Therefore, intermediate explanations have been put forward. For example, Miller and Low [63], and Avena and De Pauli [31], postulate that a small part of the structural charge is not neutralized by cations, which results in the permanent negative ζ potential.

Calculation of the edge potential of smectites is often based on an arithmetic mean sum of the charges of mixed oxides, mostly quartz or silica and alumina. Several calculations were proposed: IEP$_{\text{edge}}$ = 1/2(IEP$_{\text{quartz}}$ + IEP$_{\text{alumina}}$) [46], or ζ$_{\text{edge}}$ = 1/3(ζ$_{\text{quartz}}$ + 2ζ$_{\text{alumina}}$) [62]. Despite markedly different hypotheses, the estimations of the position of the IEP of the edge faces always fall around pH 7 [66]. Such simple assumptions neglect the real stoichiometry of edge sites. A weighed sum would read as ζ$_{\text{edge}}$ = 2/3ζ$_{\text{quartz}}$ + 1/3ζ$_{\text{alumina}}$, which would give an IEP close to pH 3.6 [65]. A similar assumption was made to model the electrokinetic potential of talc [67], which is devoid of lattice charge and displays an IEP at pH 3.3 (Fig. 6).

5. Conclusion

Analysis of the literature devoted to the acid–base properties of clays shows that many technical and theoretical difficulties are encountered, which result in strongly scattered potentiometric data, according to the experimental procedures followed by the authors. Several causes were identified. The first one is the natural origin of clays, which requires purification prior to analysis. The critical step is the use of acids and chelatants which strongly alter the clay interface due to dissolution or interaction with dissolved species from the other minerals. A second difficulty is the complex nature of the surface charge of clays and more particularly of smectites, with a permanent structural charge and an amphoteric charge located at the edges sites of the particles which represent less than 10% of the total surface area. Therefore, the quantification of the acid–base properties of clays by potentiometric titration must take into account contributions to the proton consumption/release by several side reactions such as cation exchange and dissolution.

Nevertheless, a general trend is observed. Titration curves on montmorillonite in different ionic strengths do not display the common intersection point expected from the double-layer model applied to simple metal oxides. Understanding and modeling of this behavior with respect to the structural charge requires very accurate titration data. Due to the above experimental restrictions, such data are still lacking. The crucial parameters are (i) the purification protocol, (ii) the storage conditions of purified clays, and (iii) the analytical conditions selected for titration, such as the stability criteria or the gas atmosphere in the titration vessel.

In order to improve the quantification of the acid–base properties of clays, there is a need for systematic investigation of the effects of different experimental procedures on the obtained potentiometric data.

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References
