

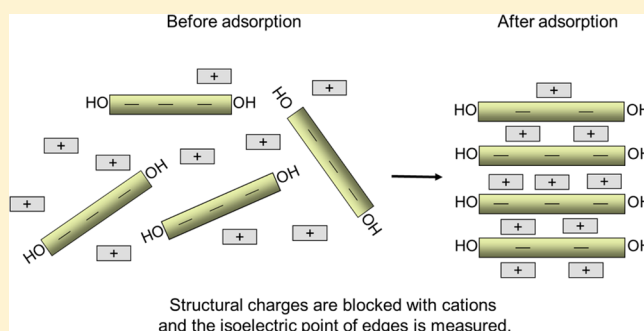
# Measuring the Isoelectric Point of the Edges of Clay Mineral Particles: The Case of Montmorillonite

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## Supporting Information

**ABSTRACT:** The isoelectric point (IEP) of the edge surface of a montmorillonite sample was determined by using electrophoretic mobility measurements. This parameter, which is fundamental for the understanding of the charging behavior of clay mineral surfaces, was never measured so far because of the presence of permanent negative charges within the montmorillonite structure, charges that mask the electrokinetic behavior of the edges. The strategy was to block or neutralize the structural charges with two different cations, methylene blue ( $\text{MB}^+$ ) and tetraethylenepentaminecopper(II) ( $[\text{Cu}(\text{tetren})]^{2+}$ ), so that the charging behavior of the particles becomes that of the edge surfaces. Adsorption isotherms of  $\text{MB}^+$  and  $[\text{Cu}(\text{tetren})]^{2+}$  at different ionic strengths (NaCl) were performed to establish the uptakes that neutralize the cation exchange capacity (CEC,  $0.96 \text{ meq g}^{-1}$ ) of the sample. At high adsorptive concentrations, there was a superequivalent adsorption of  $\text{MB}^+$  (adsorption exceeding the CEC) and an equivalent adsorption of  $[\text{Cu}(\text{tetren})]^{2+}$  (adsorption reaching the CEC). In both cases, structural charges were neutralized at uptakes very close to the CEC. Zeta potential ( $\zeta$ ) vs pH data at different ionic strengths of montmorillonite with adsorbed  $\text{MB}^+$  allowed to estimate an upper limit of the edge's IEP,  $5.3 \pm 0.2$ . The same kind of data obtained with adsorbed  $[\text{Cu}(\text{tetren})]^{2+}$  provided a lower limit of the IEP,  $4.0 \pm 0.2$ . These values are in agreement with previously informed IEP and point of zero charge of pyrophyllite, which is structurally analogous to montmorillonite but carries no permanent charges. The importance of knowing the IEP of the edge surface of clay minerals is discussed. This value characterizes the intrinsic reactivity of edges, that is, the protonating capacity of edge groups in absence of any electric field generated by structural charges. It also allows us to correct relative edge charge vs pH curves obtained by potentiometric titrations and to obtain the true edge charge vs pH curves at different electrolyte concentrations.



## 1. INTRODUCTION

The surface chemistry of clay mineral particles plays a key role in many agricultural, environmental and technological processes. All these processes are essentially controlled by the reactivity of surface groups and by electrostatic interactions among particles, which result from the particular charging behavior of the clay mineral surface. Clay minerals are layered silicates, usually aluminosilicates.<sup>1</sup> They are composed of very thin layers of around 1 nm thick (along *c*-axis) and up to several micrometers wide (other two axes) that stack together to form particles. In the case of montmorillonite, which is the mineral studied here, each layer is formed by two tetrahedral sheets (mainly  $\text{SiO}_4$  tetrahedra) sandwiching and coordinated to one octahedral sheet (mainly  $\text{Al}(\text{OH})\text{O}_5$  octahedra), and thus montmorillonite is classified as a 2:1 clay mineral. Isomorphic substitutions within the structure, that is, replacements of Si(IV) by Al(III) in the tetrahedral sheets, and of Al(III) by Fe(II) and Mg(II) in the octahedral sheet, result in structural negative charges within montmorillonite layers. This structural charge is independent of pH (permanent charge) and generates an important electric field and a negative electric potential at

the dominant basal surfaces, which constitute the faces of the particles.<sup>2–4</sup> In addition to this permanent charge, the surface at the edges of the particles contains reactive groups with proton adsorption–desorption properties, and thus edges can become positively or negatively charged depending on the pH of the dispersion (variable charge or pH-dependent charge).<sup>5–7</sup> This particular charging behavior, with structural charges expressed mainly at the faces and variable charges at the edges, leads to a charge heterogeneity that affects the modes of association of the layers, that is, edge-to-face, face-to-face and edge-to-edge, and controls most colloidal properties and applications of montmorillonite dispersions.<sup>7,8</sup>

The importance of identifying the pH values at which edges surfaces are positively or negatively charged has been recognized for a long time and subject of numerous publications. Most of the studies were performed by acid–base potentiometric titrations, which measure the relative

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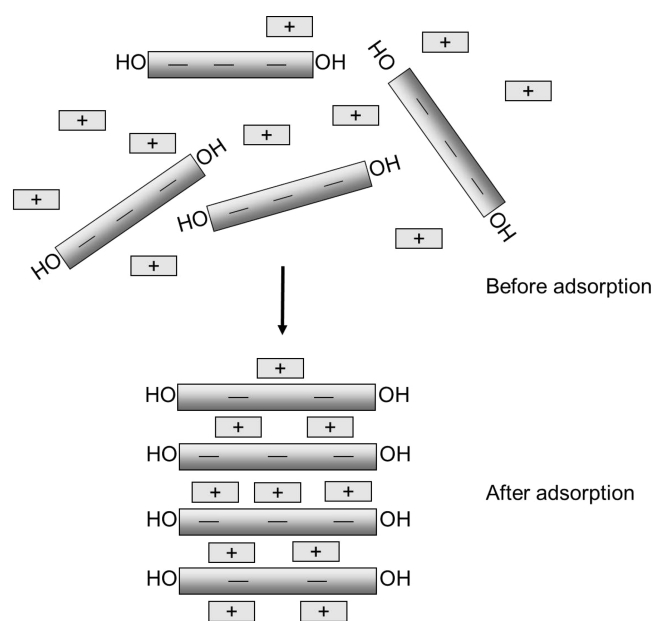
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uptake of protons at the edges.<sup>9–12</sup> An important parameter that characterizes the charging behavior of the edge surface is the point of zero charge ( $\text{pH}_{\text{PZC,edge}}$ ), which is the pH where the pH-dependent charge at edges is zero. This notation was proposed by Tombácz and Szekers,<sup>7</sup> although other notations were also used in other articles to refer to this pH value.<sup>12,13</sup> As a consequence of protonation–deprotonation reactions, below the  $\text{pH}_{\text{PZC,edge}}$  the edge surface acquires a net positive charge because positively charged surface groups exceed negatively charged ones. Above the  $\text{pH}_{\text{PZC,edge}}$  the opposite effect is observed and the edge surface acquires a net negative charge. The main problem of measuring the edge charge at different pH by acid–base titrations is that only relative charge values can be obtained,<sup>10–12</sup> and thus only apparent  $\text{pH}_{\text{PZC,edge}}$  values are assessed. The true charge density can only be quantified if the net charge at the beginning of a titration experiment is known.<sup>10</sup> Unfortunately, this initial charge was not measured so far and cannot be unambiguously and independently determined from simulations or modeling potentiometric titrations data of clay minerals.<sup>11</sup> In spite of this problem, it is nowadays accepted from relative edge charge measurements that the  $\text{pH}_{\text{PZC,edge}}$  depends on the supporting electrolyte concentration when structural negative charges are present in the solid, decreasing as the electrolyte concentration increases.<sup>6,7,9–11,14</sup> The physicochemical explanation to this behavior is that structural charges not only affect the electric potential at basal surfaces but also at edge surfaces.<sup>6,11,13</sup> Therefore, even though the edge charge is zero at the  $\text{pH}_{\text{PZC,edge}}$ , the electric potential at the edge surface remains negative due to the presence of structural charges, and changes in ionic strength modify the electrostatic screening and shift the  $\text{pH}_{\text{PZC,edge}}$ . These findings can be deduced using different electrical double layer models of the clay mineral–water interface<sup>5,6,10</sup> and were also confirmed by Delhorme et al.<sup>11</sup> using a Monte Carlo method. In addition, these last authors clearly showed that the  $\text{pH}_{\text{PZC,edge}}$  of clay minerals becomes independent of the electrolyte concentration under two different conditions: when the structural charge is absent, or when the structural charge is blocked or neutralized by interlayer cations. The first condition is the case of pyrophyllite, which is a clay mineral structurally analogous to montmorillonite but without permanent structural charges. The experimental value of  $\text{pH}_{\text{PZC,edge}}$  for pyrophyllite is around 4.2 and is independent of the ionic strength.<sup>15</sup> The second condition is the case of clay mineral particles formed by the stacking of layers containing cations in the interlayer spacing.<sup>11</sup> When large stacks are formed, the structural charge is blocked by interlayer cations and the effects of structural charges on the reactivity of edge groups are neutralized. With the structural charge neutralized, the edge surface behaves as that of a solid bearing only pH-dependent charges, and thus large montmorillonite stacks should have a  $\text{pH}_{\text{PZC,edge}}$  independent of the electrolyte concentration.<sup>11</sup>

The charging behavior of clay mineral particles is also usually investigated by measuring their electrophoretic mobility. This mobility can be related to the zeta potential,  $\zeta$ , which is the electric potential in the double layer at the location of the slipping plane.<sup>16</sup> Particles bearing only pH-dependent charges have respectively negative, zero or positive  $\zeta$  at pH values where the net charge of the particles is negative, zero or positive. The pH where  $\zeta = 0$  is usually defined as the isoelectric point (IEP). Clay minerals bearing a structural charge that exceeds in magnitude the pH-dependent charge

have electrokinetic properties dominated by the structural charge. In fact, montmorillonite particles have a negative  $\zeta$  at all studied pH and no IEP is observed.<sup>17–20</sup> Even at pH values where the edge charge could be zero or positive, the dominating effect of the structural charge results in negative zeta potentials. Some authors have theoretically estimated the IEP of edge surfaces,  $\text{pH}_{\text{IEP,edge}}$ , with simple arithmetic calculations. Durán et al.<sup>17</sup> assumed that  $\zeta$  at edges of montmorillonite should be related to those of silica and alumina given the similarity between surface groups, and used the equation  $\zeta_{\text{edge}} = 1/3 (\zeta_{\text{quartz}} + 2 \zeta_{\text{alumina}})$  obtaining a theoretical  $\text{pH}_{\text{IEP,edge}}$  close to 7. Thomas et al.,<sup>21</sup> on the other hand, assumed that the edge surface of montmorillonite contains two parts of silica (with IEP close to 2) and one part of alumina (with IEP close to 7), whose weighted sum yields a  $\text{pH}_{\text{IEP,edge}}$  close to 3.6. These simple theoretical estimations were never checked with experiments, mainly because measuring the  $\text{pH}_{\text{IEP,edge}}$  of montmorillonite is not a simple task as a consequence of the presence of structural charges. One possible way of “measuring” the  $\text{pH}_{\text{IEP,edge}}$  of montmorillonite is performing electrophoresis to a clay mineral that is structurally analogous to montmorillonite, but carrying no structural charge, such as pyrophyllite. Although data in the literature are very scarce, the work by Xia et al.<sup>22</sup> indicates that the IEP of pyrophyllite is around 3, and this value should correspond to the  $\text{pH}_{\text{IEP,edge}}$ . The disadvantage of this type of measurements is evident: experiments have to be performed with a montmorillonite substitute instead of a real montmorillonite sample. In view of the calculations by Delhorme et al.<sup>11</sup> with montmorillonite stacks, another possible and promising way of determining the  $\text{pH}_{\text{IEP,edge}}$  of montmorillonite consists in blocking or neutralizing the structural charges with an adsorbed cation, so that the charging behavior of the particles becomes that of the edge surfaces. The strategy to follow is schematized in Figure 1. A cation having high affinity for basal surfaces is adsorbed on montmorillonite in order to form stacks of layers



**Figure 1.** Schematic formation of a stack of montmorillonite layers (large rectangles) with cations (small rectangles). Edge groups of montmorillonite layers are denoted as OH. Only the case of  $\text{MB}^+$  under conditions of structural charge neutralization is represented.

with cations located in the interlayer spacing and on the external basal surfaces. Under these conditions, cations remain immobilized in the stacks, screening the structural charges and leaving only surface groups at edges. The stacks will then behave as particles bearing only pH-dependent charges and their electrokinetic behavior could be investigated as a function of pH and supporting electrolyte concentration. The IEP of these montmorillonite stacks will correspond to the  $\text{pH}_{\text{IEP,edge}}$  of montmorillonite. As far as we know, there is only one article in the literature where this strategy was applied to evaluate the electrophoretic mobility of clay minerals.<sup>21</sup> Although the aim in that article was to systematically examine the effect of layer charge on the electrophoretic mobility of different smectites, one of the studied samples was a montmorillonite treated at 300 °C with Cu(II) in order to block structural charges. This sample, with a quasi complete charge reduction by thermally induced Cu migration, had an IEP of around 2.5. Although this value is quite close to that found for pyrophyllite and also rather similar to the theoretical value of 3.6 as calculated by Thomas et al.<sup>21</sup> assuming that surface groups at edges are a mix of silica and alumina groups, the remarkable scarcity of data about the IEP of clay mineral edges indicates that more research is needed in this respect.

The aim of this article is to evaluate the isoelectric point of the edges of montmorillonite particles by blocking the structural charges of the clay mineral with two different cations, methylene blue ( $\text{MB}^+$ ) and tetraethylenepentaminecopper(II) ( $[\text{Cu}(\text{tetren})]^{2+}$ ), and measuring the electrophoretic mobility of the formed stacks at different pH and supporting electrolyte concentrations. Both cations are known to have a high affinity for montmorillonite surfaces and can enter the interlayer space blocking the structural charges.<sup>23–27</sup> A systematic study with adsorption isotherms and electrophoretic mobilities of samples with different cation loadings is presented, giving important information about the charging behavior of edge surfaces of montmorillonite.

## 2. MATERIALS AND METHODS

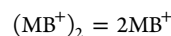
The studied montmorillonite was obtained from Northern Patagonia, Argentina. Its chemical composition and some physicochemical properties were already reported by Lombardi et al.<sup>28</sup> and correspond to the sample identified as sample 4 in that article. The material is composed mainly of montmorillonite (98% purity) with low amounts of gypsum and quartz (<2%), having a cation exchange capacity (CEC) of 0.96 meq  $\text{g}^{-1}$ , as measured by the standard ammonium acetate method, a specific surface area of 738  $\text{m}^2 \text{g}^{-1}$ , as determined by water adsorption,<sup>28</sup> and a BET surface area of 2  $\text{m}^2 \text{g}^{-1}$  as measured by  $\text{N}_2$  adsorption.

Homoionic Na-montmorillonite was prepared using a batch procedure. Particles with nominal diameter <2  $\mu\text{m}$  were obtained by sedimentation and saturated with  $\text{Na}^+$  by washing (successive centrifugal treatments) with a 1 M NaCl solution. After that, the sample was washed with 0.01 M NaCl until the conductivity of the supernatant was equal to that of the washing solution. A final stock suspension of 12.8  $\text{g L}^{-1}$  was obtained after these treatments.

Methylene Blue (Cicarelli, Argentina), as chloride salt form,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , NaCl, NaOH, HCl (all Anhedra, Argentina) and tetraethylenepentamine ( $\text{C}_8\text{H}_{23}\text{N}_5$ , Merck, Germany) were all analytical grade and were used as received.

$\text{MB}^+$  adsorption isotherms were carried out at pH 6.5 and three different ionic strengths ( $10^{-4}$ ,  $10^{-3}$  and  $10^{-2}$  M NaCl) using 15 mL polyethylene centrifuge tubes. Ten mL of the corresponding NaCl solution, 0.1 mL of the montmorillonite stock suspension, and the desired volume (from 0 to 1 mL) of a  $2.28 \times 10^{-3}$  M  $\text{MB}^+$  solution were mixed in the tubes. After intermittent sonication and overnight

shaking, they were centrifuged and the supernatants filtered with 0.22- $\mu\text{m}$ -pore acetate membranes to achieve complete separation of particles from the liquid phase.  $\text{MB}^+$  concentrations remaining in the supernatants were spectrophotometrically measured by recording the UV/vis spectra in the 200–800 wavelength range and reading the absorbance at 664 nm. Following Bergmann and O’Konski,<sup>23</sup> the absorption spectra of aqueous  $\text{MB}^+$  solutions were interpreted quantitatively as a monomer–dimer equilibrium with a molar extinction coefficient of  $9.50 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  and  $2.52 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  for monomer and dimer respectively, and a dimer dissociation constant,  $K = 1.7 \times 10^{-4}$ , for the equilibrium



The adsorbed amount of  $\text{MB}^+$  was determined as the difference between the initial concentration of  $\text{MB}^+$  and its final concentration in the supernatant. An extra isotherm was obtained at pH 4.0, adsorbing  $\text{MB}^+$  at pH 6.5 as indicated above, decreasing the pH at 4.0 with HCl, and allowing to equilibrate before centrifugation/filtration. In all experiments, and before any measurement, the glassware was carefully rinsed with the corresponding  $\text{MB}^+$  solution in order to avoid any effect of  $\text{MB}^+$  adsorption on glass.

An analogous procedure was followed to perform  $[\text{Cu}(\text{tetren})]^{2+}$  adsorption isotherms at pH 6.5 in  $10^{-4}$ ,  $10^{-3}$  and  $10^{-2}$  M NaCl. A 0.01 M  $[\text{Cu}(\text{tetren})]^{2+}$  solution was prepared by mixing equal volumes of 0.02 M  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and 0.02 M tetraethylenepentamine.<sup>25</sup> Then, 10 mL of the corresponding NaCl solution, 0.1 mL of the montmorillonite stock suspension, and the desired volume (from 0 to 0.8 mL) of the  $[\text{Cu}(\text{tetren})]^{2+}$  solution were added to each centrifuge tube. After 3 h equilibration with intermittent sonication and shaking, the suspension was centrifuged, the supernatant carefully removed and the  $[\text{Cu}(\text{tetren})]^{2+}$  concentration measured by recording the UV/vis spectra, reading the absorbance at 600 nm, and using a molar extinction coefficient of  $170 \text{ M}^{-1} \text{ cm}^{-1}$ .<sup>29</sup> An extra isotherm was obtained at pH 4.0, adsorbing the complex at pH 6.5 as indicated above, decreasing the pH at 4.0 with HCl, and allowing to equilibrate before centrifugation.

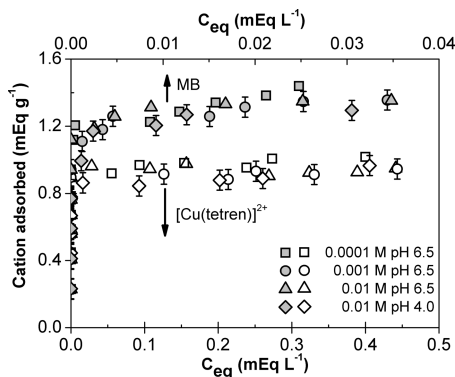
Spectrophotometric quantifications were done with an Agilent 8453 diode-array UV/vis spectrometer using a 1-cm quartz cell.

A Malvern Nano ZS90 equipment was used for measuring the electrophoretic mobility of montmorillonite particles at 25.0 °C.  $\zeta$  data were automatically calculated with the Smoluchowski equation. Two different types of measurements were performed: a)  $\zeta$  at different  $\text{MB}^+$  or  $[\text{Cu}(\text{tetren})]^{2+}$  concentrations and constant pH, and b)  $\zeta$  at different pH and constant uptakes of  $\text{MB}^+$  or  $[\text{Cu}(\text{tetren})]^{2+}$ . In the first case, centrifuge tubes containing montmorillonite and variable amounts of  $\text{MB}^+$  or  $[\text{Cu}(\text{tetren})]^{2+}$  were prepared as for adsorption isotherms measurements. After equilibration and pH checking ( $6.5 \pm 0.2$ ), the tubes were sonicated and  $\zeta$  was measured. This kind of measurements allows plotting either  $\zeta$  vs added  $\text{MB}^+$  or  $[\text{Cu}(\text{tetren})]^{2+}$  or, in combination with adsorption isotherms,  $\zeta$  vs adsorbed  $\text{MB}^+$  or  $[\text{Cu}(\text{tetren})]^{2+}$ . In the second case ( $\zeta$  vs pH measurements), 200 mL of a 0.128  $\text{g L}^{-1}$  montmorillonite suspension in NaCl and a desired amount of  $\text{MB}^+$  or  $[\text{Cu}(\text{tetren})]^{2+}$  were prepared. A 50 mL aliquot of this suspension was then equilibrated at the selected ionic strength under sonication, continuous stirring and  $\text{N}_2$  bubbling in a cylindrical, water-jacketed reaction vessel, and finally the pH was lowered to a value between 3.5 and 5 (starting pH) with a small addition of HCl. After 10 min equilibration,  $\zeta$  was measured. The pH was then increased to the desired value by a small addition of NaOH and  $\zeta$  again measured. This procedure (pH increase and  $\zeta$  measurement) was repeated until the pH of the dispersion was around 9.5. In some cases, and in order to check the reversibility of the measurements, the same suspension was backtitrated with HCl and  $\zeta$  measured after each HCl addition. This kind of measurement allows plotting  $\zeta$  vs pH curves for a given adsorbed amount of  $\text{MB}^+$  or  $[\text{Cu}(\text{tetren})]^{2+}$  at the selected ionic strength. In order to minimize changes in ionic strength by HCl and NaOH additions, starting pHs were around 5, 4, and 3.5 for measurements performed in  $10^{-4}$ ,  $10^{-3}$  and  $10^{-2}$  M NaCl respectively. The standard error in  $\zeta$  measurements was  $\pm 4$  mV.

The Malvern Nano ZS90 equipment was also used to measure the particle size distribution of 0.128 g L<sup>-1</sup> montmorillonite dispersions with and without adsorbed MB<sup>+</sup>.

### 3. RESULTS AND DISCUSSION

MB<sup>+</sup> adsorption isotherms at pH 6.5 at three different ionic strengths, and at pH 4.0 in 10<sup>-2</sup> M NaCl are shown in Figure 2.



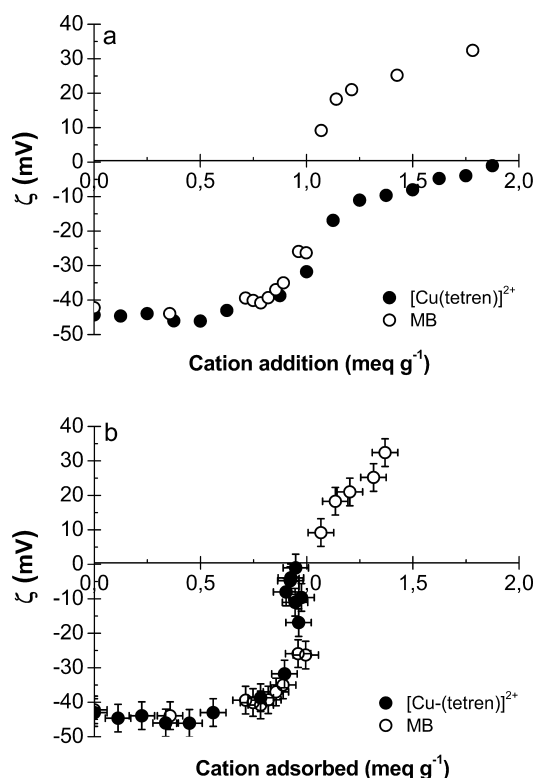
**Figure 2.** MB<sup>+</sup> and [Cu(tetren)]<sup>2+</sup> adsorption isotherms on montmorillonite. Shapes represent the different supporting electrolyte (NaCl) concentrations used, as shown in the key. Cation adsorbed represents adsorbed amounts of either MB<sup>+</sup> or [Cu(tetren)]<sup>2+</sup>, and C<sub>eq</sub> is their corresponding equilibrium concentration in the supernatant.

All curves coincide within experimental error ( $\pm 0.05$  meq g<sup>-1</sup>) indicating a negligible effect of electrolyte ions and pH on MB<sup>+</sup> adsorption. A very steep adsorption takes place up to uptakes of around 1.0 meq g<sup>-1</sup>, and then adsorption continues with a lower slope, reaching uptakes of 1.4 meq g<sup>-1</sup>. This adsorption behavior of MB<sup>+</sup> on montmorillonite is rather well known and has been reported in several articles.<sup>23,27</sup> Bergmann and O'Konski<sup>23</sup> found that the first part of the isotherm coincided completely with the ordinate axis (colorless supernatants) indicating that all MB<sup>+</sup> was bound to the surface. They interpreted this behavior as an irreversible ion exchange, where MB<sup>+</sup> adsorbed to neutralize the CEC of the sample. The other part of the isotherm was interpreted as a physical adsorption process, different to cation exchange. They also reported that aggregation of MB<sup>+</sup> took place at the montmorillonite surface. Similar conclusion were drawn by Rytwo et al.,<sup>30</sup> who found that for total dye concentration up to the CEC of the clay mineral all MB<sup>+</sup> was adsorbed and an equivalent amount of cations (Na<sup>+</sup> and Ca<sup>2+</sup>) was released from the surface, indicating ion exchange. At higher dye concentrations, MB<sup>+</sup> adsorption increased over the CEC without increasing the release of cations from the surface. Results presented in Figure 2 and those informed by Bergmann and O'Konski<sup>23</sup> and Rytwo et al.<sup>30</sup> are all coincident and point toward a high affinity adsorption of MB<sup>+</sup> up to the CEC of montmorillonite and a weaker adsorption in the second part of the isotherm. The fact that aggregation of MB<sup>+</sup> molecules takes place upon adsorption on montmorillonite and other clay minerals is also well-known,<sup>31–36</sup> and this aggregation may drive the superequivalent adsorption (adsorption exceeding the CEC) of MB<sup>+</sup>. Super-equivalent adsorption also occurs with inorganic cations such as Ca(II) ions adsorbing on solid surfaces, what is called overcharging,<sup>37</sup> although the mechanism may be different. It must be also stated that montmorillonite dispersions were rather stable for no or low MB<sup>+</sup> additions, very unstable (with the formation of large stacks or aggregates) for MB<sup>+</sup> additions

around the CEC, and again stable for MB<sup>+</sup> additions exceeding significantly the CEC. The same observation was informed by Bergmann and O'Konski.<sup>23</sup> This is illustrated by size distribution curves shown in Figure S1 (Supporting Information). In absence of MB<sup>+</sup>, montmorillonite showed a unimodal distribution ranging from 0.22 to 0.83  $\mu$ m with a peak at 0.40  $\mu$ m. For montmorillonite with 0.20 meq g<sup>-1</sup> of adsorbed MB<sup>+</sup>, a bimodal distribution was observed, with one peak (main) at 0.53  $\mu$ m and another peak (small) at 5.56  $\mu$ m. A rather similar size distribution was found for montmorillonite with 0.38 meq g<sup>-1</sup> of adsorbed MB<sup>+</sup>. At higher MB<sup>+</sup> uptakes there was a strong flocculation that impeded to perform size distribution measurements because the size of the particles was larger than the upper limit detected by the equipment (6  $\mu$ m). Indeed, large stacks and flocks could be observed even with the naked eye under these conditions. Size distribution could be again measured for MB<sup>+</sup> uptakes significantly higher than the CEC, and for example a bimodal distribution curve with one peak (main) at 0.71  $\mu$ m and another peak (small) at 5.56  $\mu$ m was again obtained with the solid having 1.13 meq g<sup>-1</sup> of adsorbed MB<sup>+</sup>.

[Cu(tetren)]<sup>2+</sup> adsorption isotherms at pH 6.5 at the three studied ionic strengths, and at pH 4.0 in 10<sup>-2</sup> M NaCl are also shown in Figure 2. As it occurred with MB<sup>+</sup>, no special trend with electrolyte concentration or pH was observed. The isotherms have the shape of high affinity isotherms, where the first part of the curves coincides with the ordinate axis and then they become rather flat and almost parallel to the abscissa. All data points of this last part of the isotherms scatter around  $0.95 \pm 0.06$  meq g<sup>-1</sup>. The dispersions were very unstable under this condition and large stacks could also be observed. As far as we know, there is no article in the literature with [Cu(tetren)]<sup>2+</sup> adsorption isotherms to compare with those of Figure 2. However, since the maximum [Cu(tetren)]<sup>2+</sup> adsorption is very similar to the CEC of the adsorbing clay mineral, and in view of the high affinity characteristics of the isotherms, it is likely that a strong adsorption takes place to reach uptakes very close to the CEC already at low [Cu(tetren)]<sup>2+</sup> concentrations. In fact, adsorption of [Cu(tetren)]<sup>2+</sup> or another similar cation, [Cu(trien)]<sup>2+</sup>, has been proposed<sup>25</sup> and used<sup>38,39</sup> as a rapid and reliable method to determine CEC on clay minerals.

Figure 3 shows the electrokinetic behavior of montmorillonite at constant pH in the presence of variable amounts of MB<sup>+</sup> and [Cu(tetren)]<sup>2+</sup>.  $\zeta$  data as a function of either added MB<sup>+</sup> or added [Cu(tetren)]<sup>2+</sup> are shown in Figure 3a. In the case of MB<sup>+</sup>, experimental points describe an S-shaped curve starting with a negative  $\zeta$  (-42 mV) in absence of MB<sup>+</sup>, which is normal for montmorillonite in NaCl,<sup>18,19,40,41</sup> and finishing with a positive  $\zeta$  (30 mV) at high MB<sup>+</sup> additions. An abrupt change in the sign of  $\zeta$  is observed, and the curve crosses the x-axis (corresponding to  $\zeta = 0$ ) at 1.0 meq g<sup>-1</sup> of added MB<sup>+</sup>. In the case of [Cu(tetren)]<sup>2+</sup>, the curve looks somewhat different.  $\zeta$  is always negative irrespective of the amount of complex added. Even though there is a significant decrease (absolute magnitude) in  $\zeta$  at high [Cu(tetren)]<sup>2+</sup> additions, no reversal of  $\zeta$  sign from negative to positive can be observed. The results for both cations can be understood if  $\zeta$  is plotted as a function of the adsorbed amounts of MB<sup>+</sup> and [Cu(tetren)]<sup>2+</sup> (Figure 3b). As a consequence of MB<sup>+</sup> adsorption,  $\zeta$  changes as adsorption increases, becomes zero at a MB<sup>+</sup> adsorption of 1.0 meq g<sup>-1</sup>, and then becomes increasingly positive at higher uptakes. It is clear that superequivalent adsorption of MB<sup>+</sup> on montmor-



**Figure 3.**  $\zeta$  of montmorillonite as a function of (a) cation addition and (b) cation adsorbed  $\text{MB}^+$  and  $[\text{Cu}(\text{tetren})]^{2+}$ . Units are expressed as meq of added or adsorbed cation per gram of montmorillonite. NaCl 0.01M, pH  $6.5 \pm 0.2$ . Error bars are only given for some curves for clarity. The same error bars correspond to all other  $\zeta$  data.

illonite occurs at high uptakes, making  $\zeta$  become positive. In the case of  $[\text{Cu}(\text{tetren})]^{2+}$ , adsorption also changes  $\zeta$  up to a value of  $-2$  mV at an adsorbed amount close to  $0.95$  meq  $\text{g}^{-1}$ . In a meq  $\text{g}^{-1}$  basis, adsorbed  $[\text{Cu}(\text{tetren})]^{2+}$  has the same charge-neutralizing power as adsorbed  $\text{MB}^+$ , as can be deduced from the coincidence of the curves in the negative  $\zeta$  side of the figure. Due to the fact that  $0.95$  meq  $\text{g}^{-1}$  is the maximum  $[\text{Cu}(\text{tetren})]^{2+}$  uptake by montmorillonite, no positive  $\zeta$  can be reached, meaning that no superequivalent adsorption of the complex takes place. Note in Figure 3b that a very small change in  $[\text{Cu}(\text{tetren})]^{2+}$  adsorption was enough to produce a large change in  $\zeta$  from  $-30$  mV to  $-2$  mV, demonstrating again that  $\zeta$  is very sensitive to changes in cation adsorption under conditions close to charge neutralization. The mentioned change in  $\zeta$  from  $-30$  mV to  $-2$  mV was obtained by increasing significantly  $[\text{Cu}(\text{tetren})]^{2+}$  addition from  $1.0$  meq  $\text{g}^{-1}$  to nearly  $2.0$  meq  $\text{g}^{-1}$  (Figure 3a). This implies that a very minor fraction of structural charge sites could be only neutralized at relatively large additions of the complex.

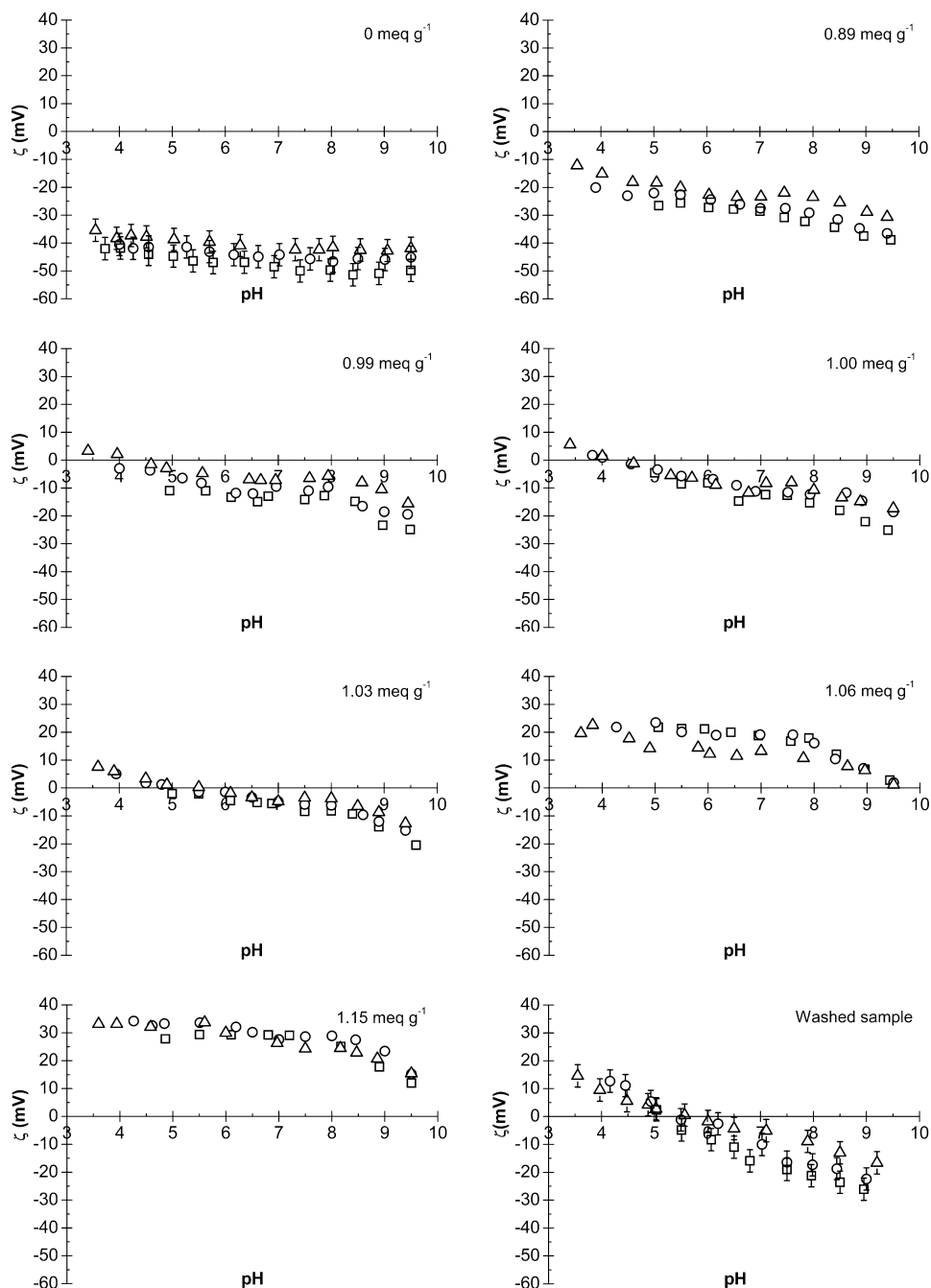
Adsorption isotherms and electrokinetic data reveal that  $\text{MB}^+$  is capable of not only blocking structural charges but also adsorbing in excess to the CEC and in excess to any charge that could be developed at the edges by protonation–deprotonation of reactive groups. In fact, if the CEC value of  $0.96$  meq  $\text{g}^{-1}$  is taken as a reasonable value for the structural charge of the studied montmorillonite sample, the measured  $\text{MB}^+$  uptake of  $1.4$  meq  $\text{g}^{-1}$  at high  $\text{MB}^+$  concentrations exceeds by 46% the structural charge. This excess, in addition, is higher than the usually assumed<sup>11</sup> or measured<sup>42</sup> variable charges in smectites. Therefore, if the strategy to measure the  $\text{pH}_{\text{IEP,edge}}$  of

montmorillonite is to block structural charges by adsorbing an equivalent amount of  $\text{MB}^+$  and measuring  $\zeta$  as a function of pH, the amount of  $\text{MB}^+$  added to a montmorillonite suspension should be carefully chosen. Two different procedures of blocking structural charges with  $\text{MB}^+$  could be explored: (a) adding  $\text{MB}^+$  to produce an adsorption that equals the CEC of the sample; and (b) adsorbing first  $\text{MB}^+$  in excess at high concentrations and desorbing afterward the  $\text{MB}^+$  that exceeds the CEC by successive washings with supporting electrolyte. This second procedure is based on the suggestion by Bergmann and O’Konski<sup>23</sup> that  $\text{MB}^+$  adsorption up to the CEC is irreversible. It can be anticipated that none of these procedures guarantees success, mainly because of the abrupt change in  $\zeta$  that takes place for  $\text{MB}^+$  uptakes around the CEC. A difference in the addition of  $\text{MB}^+$  of  $\pm 0.06$  meq  $\text{g}^{-1}$  (the uncertainty in the measurement of the CEC) will make  $\zeta$  to jump from negative to positive values at pH  $6.5 \pm 0.2$ , and thus a very large uncertainty in the  $\text{pH}_{\text{IEP,edge}}$  will be obtained after measuring  $\zeta$  vs pH curves. Similar problems arise for a washing treatment aiming to desorb all the  $\text{MB}^+$  that exceeds the CEC. Any washing treatment that is not perfect, that is, insufficient washing due to a slow desorption reaction, will leave the surface with some extra and undesired  $\text{MB}^+$  molecules, impacting significantly on the measured  $\text{pH}_{\text{IEP,edge}}$ .

Figure 4 illustrates the difficulties mentioned above. It shows  $\zeta$  vs pH curves at three different ionic strengths for montmorillonite with different uptakes of  $\text{MB}^+$ . For  $0$  meq  $\text{g}^{-1}$  uptake, that is, pure montmorillonite,  $\zeta$  is always negative and there is a very small effect of pH and ionic strength. The behavior is well-known for this mineral in NaCl.<sup>5,19,21,40,41</sup>  $\zeta$  is dominated by the negative structural charge of the clay mineral, and the small decrease as pH decreases is probably caused by protonation of edge groups, which are minor in comparison with the structural charge. The decrease in  $\zeta$  (absolute value) as the electrolyte concentration increases is a known double layer effect on charged solid–liquid interfaces. For an uptake of  $0.89$  meq  $\text{g}^{-1}$ , which is already close to the CEC,  $\zeta$  is also negative at all pH but less negative than for pure montmorillonite. Even though structural charges are still dominating the behavior, the effects of pH are stronger, indicating that the participation of variable charges is significant. For uptakes of  $0.99$ ,  $1.00$ ,  $1.03$ , and  $1.06$  meq  $\text{g}^{-1}$  variable charges dominate the behavior, and isoelectric points are observed at  $4.0$ ,  $4.5$ ,  $5.0$ , and  $9.5$  respectively. For higher uptakes,  $\zeta$  is always positive at all pH, showing that the positive charge originated from the superequivalent adsorption of  $\text{MB}^+$  controls the electrokinetics. Note that a very small change in uptake from  $0.99$  to  $1.06$  meq  $\text{g}^{-1}$  makes the IEP to change from  $4.0$  to  $9.5$ , reflecting the steep slope of the curves in Figure 3 and making it very difficult to establish the actual value of the  $\text{pH}_{\text{IEP,edge}}$ .

Since  $\zeta$  vs pH measurements implied working with montmorillonite at low pH, some data could be affected by dissolution of the solid. In order to discard this, Mg(II) was measured at pH  $4.0$  by AA spectrometry and resulted to be  $1.1 \times 10^{-5}$  M, which cannot affect the ionic strength of the solutions. In addition, electrophoretic measurements of a montmorillonite suspension with adsorbed  $\text{MB}^+$  at pH  $4.0$  showed that  $\text{MgCl}_2$  additions up to  $3.7 \times 10^{-5}$  M did not produce any change in  $\zeta$  ( $-5 \pm 4$  mV), demonstrating that Mg(II) that could be released by dissolution did not affect electrokinetic results (Supporting Information Figure S2).

In order to explore the feasibility of the second proposed procedure, a washing of montmorillonite particles with



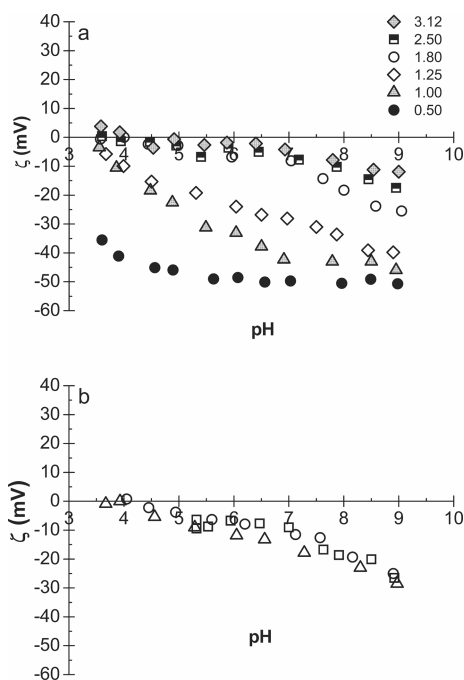
**Figure 4.**  $\zeta$  vs pH for montmorillonite with different amounts of adsorbed  $\text{MB}^+$  (indicated in each graph). NaCl concentration: squares,  $10^{-4}$  M; circles,  $10^{-3}$  M; triangles,  $10^{-2}$  M. Error bars are only given for some curves for clarity. The same error bars correspond to all other  $\zeta$  data.

adsorbed  $\text{MB}^+$  was conducted in order to remove the  $\text{MB}^+$  exceeding the CEC.  $6.4 \times 10^{-3}$  g of montmorillonite containing  $1.24 \text{ meq g}^{-1}$  of adsorbed  $\text{MB}^+$  were treated with 0.01 M NaCl as the washing solution, with sonication and further centrifugation. Twenty washings steps (1 per day) were performed at the beginning of this procedure using in each step 50 mL of the washing solution and measuring spectrophotometrically the  $\text{MB}^+$  released to the supernatants. The  $\text{MB}^+$  content of montmorillonite after these water treatments was estimated to be  $1.18 \text{ meq g}^{-1}$  and no IEP was found,  $\zeta$  being always positive at all investigated pH (not shown). The washing was then continued with 5 more steps, but using 500 mL of washing solution in each step. Unfortunately, since the release of  $\text{MB}^+$  in all these washing

experiments was very low, the dye concentration in the supernatants could not be accurately quantified, especially after the 500-mL washings. The final  $\text{MB}^+$  content after all the washings was estimated to be between 1.0 and  $1.1 \text{ meq g}^{-1}$ , and it seemed that not all the  $\text{MB}^+$  in excess to the CEC could be removed. The  $\zeta$  vs pH curves of the so-washed particles at three different ionic strengths are shown in Figure 4. A behavior typical of a material with only pH-dependent charges at the surface can be observed, with all curves crossing at the IEP, which resulted to be  $5.3 \pm 0.2$ . Since some  $\text{MB}^+$  exceeding the CEC of the clay mineral may have still remained on the particles, we believe that this is the upper limit for the  $\text{pH}_{\text{IEP,edge}}$  of montmorillonite. An alternative washing was intended with ethanol. 0.026 g of montmorillonite with  $1.05 \text{ meq g}^{-1}$  of

adsorbed  $\text{MB}^+$  were washed with ethanol (50 mL per washing step) followed by centrifugation and filtration. Even after 20 washing steps,  $\text{MB}^+$  continued being released from the solid. Adsorbed  $\text{MB}^+$  after these washing was estimated to be  $<0.90 \text{ meq g}^{-1}$ , indicating that ethanol removed more  $\text{MB}^+$  than the expected. In fact, zeta potential data of the so washed sample were always negative ( $-15$  and  $-40 \text{ mV}$ ) at the three investigated ionic strengths and pH range 4–9 (Supporting Information Figure S3). It is not clear why ethanol is able to extract a very significant amount of  $\text{MB}^+$ , but it is clear that this washing method cannot be used to exactly block structural charges.

Figure 5 shows the  $\zeta$  vs pH curves of montmorillonite in the presence of  $[\text{Cu}(\text{tetren})]^{2+}$ . In Figure 5a the curves obtained in



**Figure 5.** (a)  $\zeta$  vs pH of montmorillonite with different  $[\text{Cu}(\text{tetren})]^{2+}$  additions in  $10^{-2} \text{ M NaCl}$ . Added  $[\text{Cu}(\text{tetren})]^{2+}$  in  $\text{meq g}^{-1}$  is given. (b)  $\zeta$  vs pH of montmorillonite with  $1.80 \text{ meq g}^{-1}$  of added  $[\text{Cu}(\text{tetren})]^{2+}$ :  $\square$ ,  $10^{-4} \text{ M}$ ;  $\circ$ ,  $10^{-3} \text{ M}$ ;  $\triangle$ ,  $10^{-2} \text{ M}$ .

$0.01 \text{ M NaCl}$  for different  $[\text{Cu}(\text{tetren})]^{2+}$  additions are shown. At  $[\text{Cu}(\text{tetren})]^{2+}$  addition of  $0.50 \text{ meq g}^{-1}$  (uptake  $0.45 \text{ mEq g}^{-1}$ )  $\zeta$  is always negative and there is a small effect of pH. As the copper complex concentration increases the effects of pH become more important indicating that structural charges are being blocked and that pH-dependent charges are taking control of the behavior. At additions above  $1.80 \text{ meq g}^{-1}$  (nearly maximum uptake,  $0.95 \text{ mEq g}^{-1}$ ) all the curves show an IEP of  $4.0 \pm 0.2$ . The same IEP can be deduced from the curves performed at three different ionic strengths (Figure 5b) with an addition of  $1.80 \text{ meq g}^{-1}$ , which also corresponds to nearly maximum uptake. Data in Figure 5 shows that increasing  $[\text{Cu}(\text{tetren})]^{2+}$  additions increasingly block structural charges, shifting the IEP of the solid up to a value of  $4.0 \pm 0.2$  at high  $[\text{Cu}(\text{tetren})]^{2+}$  concentrations. Since all or nearly all structural charges are blocked under these conditions, the value  $4.0 \pm 0.2$  appears to be the lower limit of the  $\text{pH}_{\text{IEP,edge}}$  of montmorillonite.

Data presented in this article show that the  $\text{pH}_{\text{IEP,edge}}$  of montmorillonite stacks with their structural charges blocked

with either  $\text{MB}^+$  or  $[\text{Cu}(\text{tetren})]^{2+}$  is between  $4.0 \pm 0.2$  and  $5.3 \pm 0.2$ . Since under these conditions the stacks behave as solids bearing only pH-dependent charges, and as it occurs with this kind of solids in an indifferent electrolyte such as  $\text{NaCl}$ , the measured isoelectric point should be also equal to the  $\text{pH}_{\text{PZC,edge}}$ . This value of  $\text{pH}_{\text{IEP,edge}} = \text{pH}_{\text{PZC,edge}}$  is quite close to previously found isoelectric points or points of zero charge of pyrophyllite and also close to the value of 3.6 that results from calculations by Thomas et al.<sup>21</sup>

#### 4. IMPORTANCE OF KNOWING THE VALUE $\text{pH}_{\text{IEP,EDGE}} = \text{pH}_{\text{PZC,EDGE}}$

The value  $\text{pH}_{\text{IEP,edge}} = \text{pH}_{\text{PZC,edge}}$  is a fundamental parameter of the clay mineral surface because it characterizes the intrinsic reactivity of edges, i.e. the protonating capacity of edge groups in absence of any electric field generated by structural charges. Hereon, this pH value will be called the intrinsic point of zero charge of edges,  $\text{pH}_{\text{PZC,edge}}^{\text{int}}$ . If the edge surface is assumed to be populated with only one type of protonable group, as it is normally proposed with the 1-pK model,<sup>43,44</sup> the protonation reaction can be written as:



where  $\text{A}^{-1/2}$  and  $\text{AH}^{+1/2}$  denote respectively the unprotonated and protonated surface groups. The mass action law of this reaction can be written as:

$$K_{\text{H}}^{\text{int}} e^{-F\psi_{\text{edge}}/RT} = \frac{\{\text{AH}^{+1/2}\}}{\{\text{A}^{-1/2}\}(\text{H}^+)} \quad (2)$$

or in a logarithmic and rearranged form

$$\text{pH} = \log K_{\text{H}}^{\text{int}} - \log \frac{\{\text{AH}^{+1/2}\}}{\{\text{A}^{-1/2}\}} - F\psi_{\text{edge}}/2.3RT \quad (3)$$

where  $K_{\text{H}}^{\text{int}}$  is the intrinsic protonation constant of reaction 1,  $\{\text{A}^{-1/2}\}$  and  $\{\text{AH}^{+1/2}\}$  are the surface concentrations of the groups,  $\psi_{\text{edge}}$  is the surface potential at the edges,  $(\text{H}^+)$  is the proton activity in the bulk solution, and  $R$  and  $T$  have their usual meaning. In the cases of clay minerals with no structural charges, or montmorillonite stacks with all structural charges blocked by cations, at the point of zero charge of edges (being  $\text{pH}_{\text{PZC,edge}}^{\text{int}}$  in these two considered cases) the following equalities hold:  $\{\text{AH}^{+1/2}\} = \{\text{A}^{-1/2}\}$  and  $\psi_{\text{edge}} = 0$ , thus eq 3 becomes

$$\text{pH}_{\text{PZC,edge}}^{\text{int}} = \log K_{\text{H}}^{\text{int}} \quad (4)$$

Although for simplicity eq 4 is deduced here for an edge surface populated only with  $\text{A}^{-1/2}$  and  $\text{AH}^{+1/2}$  groups, it can be also deduced for surfaces containing amphoteric groups, such as in the case of the 2-pK model.<sup>43,44</sup> This equation shows the importance of knowing the  $\text{pH}_{\text{PZC,edge}}^{\text{int}}$  of montmorillonite, since it directly reflects the intrinsic protonation constant of edge groups.

Equation 3 is also applicable to clay mineral particles with their structural charges not blocked by cations. In this case, at the point of zero charge of edges (being  $\text{pH}_{\text{PZC,edge}}$  here) the equality  $\{\text{AH}^{+1/2}\} = \{\text{A}^{-1/2}\}$  still remains, but the electric field generated by the structural charges results in a negative electric potential at the edges, thus  $\psi_{\text{edge}} \neq 0$ . Therefore, eq 3 becomes (using also eq 4):

$$\text{pH}_{\text{PZC,edge}} = \text{pH}_{\text{PZC,edge}}^{\text{int}} - F\psi_{\text{edge}}/2.3RT \quad (5)$$

Equation 5 indicates that the  $\text{pH}_{\text{PZC,edge}}$  should increase as the negative potential at the edges increases, and explains in a simple way two important properties of the behavior of clay mineral edges. On one hand, it shows that increasing the structural negative charge of clay layers will increase the  $\text{pH}_{\text{PZC,edge}}$  as a consequence of the increasing negative field felt by edge groups. This is in agreement with Monte Carlo calculations by Delhomme et al.,<sup>11</sup> who simulated the behavior of pyrophyllite (no structural charge), montmorillonite (intermediate structural charge density) and Illite (high structural charge density). On the other hand, it also shows that for a given clay mineral with structural charges the  $\text{pH}_{\text{PZC,edge}}$  will change as the electrolyte concentration changes as a consequence of a different screening of charges by the electrolyte. In this sense, Bourg et al.<sup>10</sup> solved the Poisson–Boltzmann equation for a clay mineral particle with the layer charge ( $-0.88 \text{ meq g}^{-1}$ ) and the surface area ( $780 \text{ m}^2 \text{ g}^{-1}$ ) of the MX-80 montmorillonite sample, and calculated the reduced potential at the edge surface,  $F\psi_{\text{edge}}/RT$ , at different electrolyte concentrations. When the edge charge was zero,  $F\psi_{\text{edge}}/RT$  was around  $-0.5$ ,  $-1.9$ , and  $-3.9$  at electrolyte concentrations 0.1, 0.01 and 0.001 M, respectively. According to eq 5, these values imply that the  $\text{pH}_{\text{PZC,edge}}$  is shifted toward higher pH values by 0.22, 0.83, and 1.7 units from the  $\text{pH}_{\text{PZC,edge}}^{\text{int}}$ , and is in agreement with the relative variation of apparent  $\text{pH}_{\text{PZC,edge}}$  values published in many articles.<sup>7–9,11,12,17,21</sup>

As a corollary to the above discussion, knowing the  $\text{pH}_{\text{PZC,edge}}^{\text{int}}$  of montmorillonite allows locating the  $\text{pH}_{\text{PZC,edge}}$  of charge vs pH curves obtained by potentiometric titrations, avoiding the problems of working with “apparent” or relative values. For example, the  $\text{pH}_{\text{PZC,edge}}$  at 0.1 M electrolyte should be placed at around 0.22 pH units above the  $\text{pH}_{\text{PZC,edge}}^{\text{int}}$ , and the actual position of all the other titration curves comes automatically.

## 5. CONCLUSIONS

The blocking of structural charges with  $\text{MB}^+$  and  $[\text{Cu}(\text{tetren})]^{2+}$  made possible to measure the  $\text{pH}_{\text{IEP,edge}}$  of montmorillonite particles, parameter that could not be measured so far. Although adsorption of  $\text{MB}^+$  exceeds the CEC of the solid, a combination of adsorption isotherms, washing treatments and  $\zeta$  measurements at different pH and supporting electrolyte concentrations allowed to determine the upper limit of  $\text{pH}_{\text{IEP,edge}}$ . There was no superequivalent adsorption of  $[\text{Cu}(\text{tetren})]^{2+}$  on montmorillonite, and thus  $\zeta$  measurements at different pH and supporting electrolyte concentrations at high  $[\text{Cu}(\text{tetren})]^{2+}$  additions allowed to determine the lower limit of  $\text{pH}_{\text{IEP,edge}}$ . This measured  $\text{pH}_{\text{IEP,edge}}$  reflects the intrinsic protonation constant of edge groups and equals the  $\text{pH}_{\text{PZC,edge}}$  of montmorillonite in absence of any effect of structural charges. This is a valuable parameter to locate edge charge vs pH curves of montmorillonite obtained with potentiometric titrations. In addition, since this is an intrinsic property of the edge surface, no changes in its value are expected by changing particle size, as long as the chemical composition of the particles and the population of reactive groups at edges remain the same.

It must be finally stated that blocking structural charges with either  $\text{MB}^+$  or  $[\text{Cu}(\text{tetren})]^{2+}$  was possible because of the high affinity that both cations have for the studied solid, and because montmorillonite is an expandable clay mineral that can allocate the cations in the interlayer space, forming large stacks with structural charges neutralized. This may not be possible with

non expandable clay minerals such as kaolinite or Illite. This could be done, in principle, with other montmorillonite samples having a different layer charge than the studied here for comparison. However, since each natural sample has its own particularities, each sample will have to be thoroughly characterized and investigated in order to find the exact point where the structural charges are blocked, and to finally measure the  $\text{pH}_{\text{IEP,edge}}$ .

## ■ ASSOCIATED CONTENT

### Supporting Information

Figures S1, S2 and S3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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